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Coordination Compounds of Transition Metal Hydrazine Derivatives. Part 25. Monohydrazine-*S*-Methylcarbodithioate Schiff Bases Derived from α-Dicarbonyl Compounds

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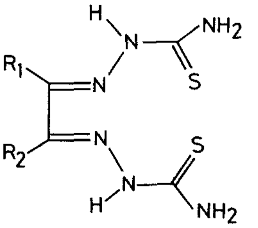
Summary

The monohydrazones derived from the condensation of diacetyl and benzil with hydrazine-*S*-methylcarbodithioate (Dahydth) and (Benhydth) were prepared and their ligation properties with nickel(II), copper(II), palladium(II), zinc(II) and cadmium(II) were studied. A series of bisligand chelates were isolated and characterized. In the zinc(II), cadmium(II) copper(II) and palladium(II) bisligand chelates, both Dahydth and Benhydth act as mononegative bidentate molecules. The Ni(Dahydth-H)$_2$ chelate possesses an octahedral structure where Dahydth acts as a mononegative tridentate ligand. The ^{1}H n.m.r. spectra of the two ligands as well as of the diamagnetic metal(II) chelates are discussed. The fragmentation in a mass spectrometer of all these chelates was also studied.

Introduction

Many bisthiosemicarbazones of α-diketones and α-ketoaldehydes possess marked carcinostatic and carcenolytic activity against several established tumours(1–5). The presence of copper(II) ion enhances both *in vitro* and *in vivo* activity of 2-ethoxy-2-oxobutyraldehyde bisthiosemicarbazone [*1*, R_1 = H, R_2 = CH(OEt)Me]. In fact, the copper(II) chelate [*2*, M = Cu^{II}, R_1 = H, R_2 = CH(OEt)Me] proved to be much more effective compared to the parent bisthiosemicarbazone(6,7). Such studies have led to increasing interest in the coordination chemistry of these bisthiosemicarbazones and a number of nickel(II), copper(II) and zinc(II) chelates with α-diketone and α-ketoaldehyde bisthiosemicarbazones were synthesized and characterized(8–18). Furthermore, Das and Livingstone(19) reported that palladium(II) and copper(II) chelates of some Schiff bases derived from hydrazine-*S*-methylcarbodithioate *(3)* display confirmed cytostatic activity in the 9 KB test system, which is an *in vitro* human epidermoid carcinoma of the nasopharynx. These findings stimulated our interest in a systematic study of the coordination chemistry of some hydrazine-*S*-methylcarbodithioate Schiff bases derived from α-diketones, α-ketoaldehydes and α-ketoacids. In the present work, the ligation properties of monohydrazones obtained from the condensation of diacetyl and benzil with hydrazine-*S*-methyl carbodithioate are discussed.



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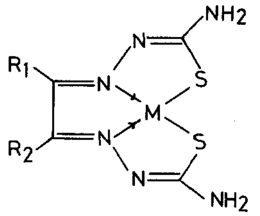

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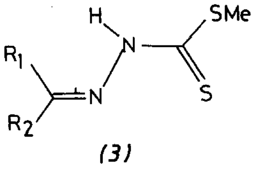

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Results and Discussion

The reaction of diacetyl (*4*, R_1, R_2 = Me) with hydrazine-*S*-methyl carbodithioate (hydth) *(5)* gives a mixture of mono- (*6*, R_1, R_2 = Me) and bishydrazone (*7*, R_1, R_2 = Me). The monohydrazone can be extracted with ethanol and recrystallized from a CHCl$_3$-light petroleum ether mixture. Phenylglyoxal (*4*, R_1 = H, R_2 = Ph), however, yields the bishydrazone (*7*, R_1 = H, R_2 = Ph) and attempts to prepare the monohydrazone were unsuccessful. With benzil, (*4*, R_1, R_2 = Ph), the monohydrazone (*6*, R_1, R_2 = Ph) is obtained as a sole product, due to steric effects of the phenyl substituents(20).

A series of zinc(II), cadmium(II), nickel(II), copper(II) and palladium(II) bisligand chelates, M(α-dikhydth-H)$_2$, have been prepared from the reaction of the monohydrazones, Dahydth (*6*, R_1, R_2 = Me) and Benhydth (*6*, R_1, R_2 = Ph) with the corresponding metal(II) acetate or chloride in ethanol. These chelates, together with their elemental analyses, are listed in Table 1.

The i.r. spectral data cited in Table 2, suggest that in zinc(II), cadmium(II), copper(II) and palladium(II) chelates

Table 1. Elemental analyses for the M(α-dikhydth-H)$_2$ chelates

Compound	Found (Calcd.)% M	N	S
Zn(Dahydth-H)$_2$	14.6 (14.7)	12.3 (12.6)	28.6 (28.8)
Cd(Dahydth-H)$_2$	22.6 (22.8)	11.2 (11.4)	25.9 (26.1)
Ni(Dahydth-H)$_2$	13.5 (13.4)	12.6 (12.8)	29.2 (29.3)
Cu(Dahydth-H)$_2$	14.4 (14.3)	12.3 (12.7)	28.5 (28.9)
Zn(Benhydth-H)$_2$	9.3 (9.5)	7.9 (8.1)	18.2 (18.5)
Cd(Benhydth-H)$_2$	14.9 (15.2)	7.4 (7.6)	17.2 (17.4)
Ni(Benhydth-H)$_2$	8.6 (8.6)	7.8 (8.2)	18.6 (18.7)
Cu(Benhydth-H)$_2$	9.3 (9.2)	7.9 (8.1)	18.5 (18.6)
Pd(Benhydth-H)$_2$	14.2 (14.5)	7.3 (7.6)	17.2 (17.5)

Dahydth and Benhydth refer to diacetyl and benzil monohydrazone Schiff bases respectively.

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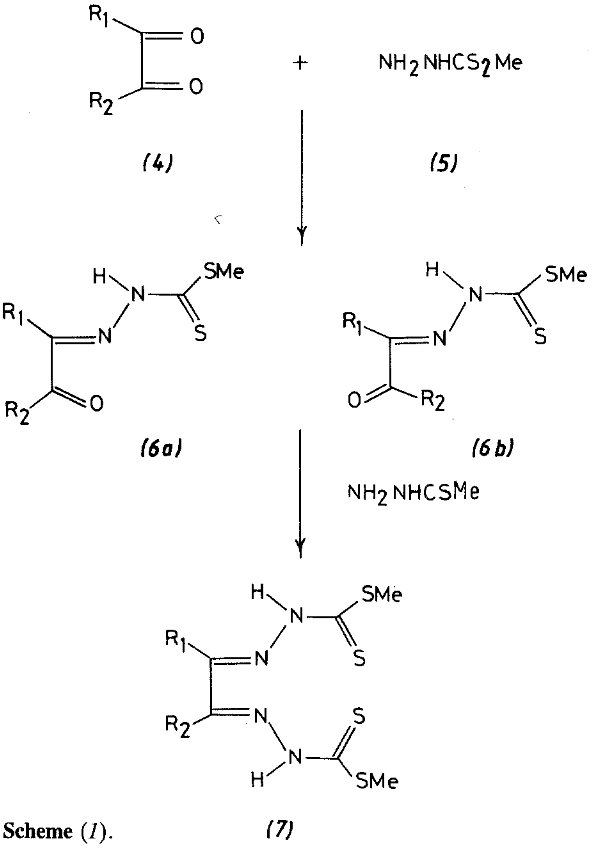
Table 2. I. r. spectra[a] of α-dicarbonyl monohydrazine-S-methyl carbodithioate Schiff bases and their metal(II) chelates

Compound	N-H	C=O	C=N	S–C=N	N–CSSMe			
Dahydth	3200	1700	1618	1490	1140	1095	975	780
Zn(Dahydth-H)$_2$	–	1680	–	1560	–	1090, 1040	970, 955	820
Cd(Dahydth-H)$_2$	–	1680	–	1480	–	1090, 1040	980, 955	818
Ni(Dahydth-H)$_2$	–	1655	1560	–	–	1095, 1050	975, 960	820
Cu(Dahydth-H)$_2$	–	1700	1620	1500	–	1070	970	780
Benhydth	3225	1660	1600, 1580	1480	–	1055	960, 930	780
Zn(Benhydth-H)$_2$	–	1680	1600, 1580	1480	–	1080, 1020	960, 920	765
Ni(Benhydth-H)$_2$	–	1680	1600, 1580	1480	–	1075, 1020	970, 910	765
Cu(Benhydth-H)$_2$	–	1680	1600, 1580	1480	–	1075, 1015	960, 910	765
Pd(Benhydth-H)$_2$	–	1680	1600, 1580	1480		1040, 1020	960, 915	765

[a] cm^{-1}.



Scheme (*1*).

of both Dahydth and Benhydth, the ligand acts as a mononegative bidentate ligand chelated to the central metal ion *via* the azomethine nitrogen and the deprotonated thiol sulphur. This fact is quite evident from the disappearance of ν(N–H) and the observed negative shift in ν(C=N), as compared to the spectra of the parent ligands. While the position of the ν(C=O) band in the i.r. spectra of M(Dahydth-H)$_2$ [M = zinc(II), cadmium(II) and copper(II)] chelates is almost unchanged, a positive shift is observed in the spectra of the corresponding Benhydth chelates. This indicates that the carbonyl oxygen is not involved in the chelation process. However, the observed positive shift in ν(C=O) frequencies of Benhydth chelates may be due to the absence of (C=O···H–N) intra-or intermolecular hydrogen bonding originally present in the parent Benhydth ligand (*6*, R_1, R_2 = Ph).

In Ni(Dahydth-H)$_2$ the ligand behaves as a mononegative tridentate ion in which the carbonyl oxygen acts as a third coordination site. This is supported by the observed negative shift ($\Delta\nu$ =45 cm^{-1}) in ν(C=O) as to the spectrum of Dahydth itself. Ni(Benhydth-H)$_2$, on the other hand, does not show such as negative shift but the ν(C=O) value suffers a positive shift ($\Delta\nu$ = 20 cm^{-1}) similar to that observed in other Benhydth chelates.

The bisligand zinc(II) and cadmium(II) chelates of both Dahydth and Benhydth are diamagnetic. Their electronic spectra, Table 3, show absorption bands due to the L–L* transition by the mononegative ion of the ligand perturbed by the central metal ion. Inspection of the data given in Table 3,

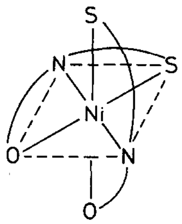
Table 3. Electronic spectra of Dahydth, Benhydth and their metal(II) chelates, M(α-dikhydth-H)$_2$

Compound	Solvent	Band max. (nm) (log ε, M^{-1} cm^{-1})
Dahydth	$CHCl_3$	250(2.58), 305sh, 322(4.45), 385sh
Zn(Dahydth-H)$_2$	$CHCl_3$	250sh, 355(4.32), 420(4.21)
Cd(Dahydth-H)$_2$	C_5H_6	355(4.31), 415(4.27), 480sh
Ni(Dahydth-H)$_2$	NM[a]	480sh, 590sh, 830sh
Ni(Dahydth-H)$_2$	$CHCl_3$	255sh, 295sh, 370(4.46), 465(4.16), 555sh, 655sh, 800(1.83), 850sh
Ni(Dahydth-H)$_2$	py	430sh, 480sh, 570sh, 800sh
Cu(Dahydth-H)$_2$	C_6H_6[a]	295, 315sh, 445sh, 575sh
Benhydth	$CHCl_3$	262(4.18), 310sh, 335(4.37)
Zn(Benhydth-H)$_2$	$CHCl_3$	257(4.47), 315(4.37), 360sh
Cd(Benhydth-H)$_2$	C_6H_6	310(4.33), 350sh
Ni(Benhydth-H)$_2$	$CHCl_3$	255(4.69), 285sh, 325sh, 390(3.89), 440sh, 570sh
Ni(Benhydth-H)$_2$	py	390sh, 500(3.94), 665sh, 800sh
Cu(Benhydth-H)$_2$	$CHCl_3$[a]	252, 310, 360sh, 440sh, 570sh, 595
Pd(Benhydth-H)$_2$	C_6H_6	300(4.44), 370sh, 480sh

[a] Nujol mull; [b] Satd. soln.

reveals that the maximum absorption bands of M(Dahydth-H)$_2$ [M = zinc(II) or cadmium(II)], are shifted to lower frequencies compared to those of Benhydth. This result can be attributed to the steric effect of the phenyl group in Benhydth which forces the benzoyl residue out-of-plane with respect to the chelate ring. However, in Dahydth chelates, the acetyl group seems to be coplanar with the chelate ring and can thus stabilize the excited state through extended conjugation. Most likely, the zinc(II) and cadmium(II) chelates with Dahydth and Benhydth ligands possess a tetrahedral structure.

Ni(Dahydth-H)$_2$ is paramagnetic (μ_{eff} = 3.00; 298 K) and its electronic spectrum, Table 3, suggests a distorted octahedral environment around the nickel(II) ion *(8)*$^{(20)}$. This result agrees with the tridentate nature of deprotonated Dahydth. However, Ni(Benhydth-H)$_2$ is diamagnetic and its electronic spectrum, Table 3, does not show any absorption beyond 750 nm, implying a square planar structure$^{(20)}$ where the Benhydth molecule acts as a bidentate ligand.



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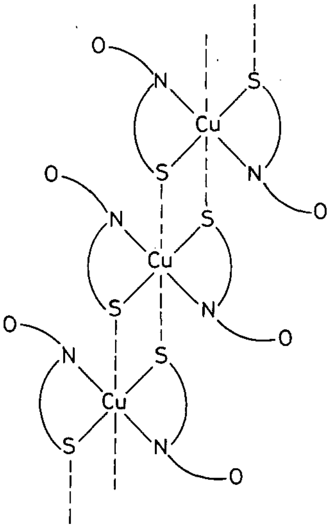

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The difference in chelation modes between Ni(Dahydth-H)$_2$ and Ni(Benhydth-H)$_2$ emphasizes the role or steric requirement of R$_1$ and R$_2$ in the monohydrazone ligands. In Benhydth (*6*, R$_1$, R$_2$ = Ph) the bulky phenyl groups favour domination of the *s-transoid* rather than the *s-cisoid* structure and the carbonyl oxygen is remote from the nickel(II) ion, while in Dahydth (*6*, R$_1$, R$_2$ = Me) the *s-cisoid* configuration can be achieved and the monohydrazone can function as a tridentate ligand. As expected, a square planar structure can also be assigned for Pd(Benhydth-H)$_2$, similar to that for the corresponding nickel(II) chelate.

In both Cu(Dahydth-H)$_2$ and Cu(Benhydth-H)$_2$, the monohydrazone molecule functions as a bidentate ligand, whereas the acyl oxygen remains uncoordinated. These chelates are paramagnetic with subnormal magnetic moments (μ_{eff} = 1.46–1.58, 298 K). It was reported$^{(21)}$ that the magnetic moments of copper(II) chelates, with the other deprotonated bidentate hydth Schiff bases *(3)*, depend on the nature of R$_1$ and R$_2$ in the ligand.

The bisligand copper(II) chelates with aromatic aldehydic Schiff bases (*3*, R$_1$ = H, R$_2$ = Ph, p-ClC$_6$H$_4$, p-MeOC$_6$H$_4$ or p-MeC$_6$H$_4$) possess a monomeric square planar structure with normal magnetic moments (μ_{eff} = *ca.* 1.80 BM; 298 K), while those derived from aliphatic, alicyclic and aromatic ketones (*3*, R$_1$, R$_2$; Me, Me; Me, Et; Et, Et; Me, CH$_2$Ph; Me, Ph; C$_5$H$_{10}$) show subnormal magnetic moments (μ_{eff} = 1.33–1.40; 298 K) and a polymeric structure was proposed for these chelates$^{(21)}$. The subnormal magnetic moments of both Cu(Dahydth-H)$_2$ and Cu(Benhydth-H)$_2$ also suggest some sort of molecular association and an analogous polymeric structure$^{(9)}$ with Cu–S bridges can be tentatively assigned for these chelates. Their electronic spectra are consistent with a tetragonal copper(II) species and show a split band centered at *ca.* 595 nm due to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, in addition to a band at 440 nm attributable to ligand-metal (S–Cu) charge transfer$^{(22)}$.

A study of the ^{1}H n.m.r. spectra of the monohydrazone ligands and their corresponding diamagnetic metal(II) chelates may also provide some evidence for the structure of these chelates. The ^{1}H n.m.r. spectra of Dahydth, Table 4, show the expected Me–C=N, Me–C=O, MeS- and N–H signals at δ = 2.16, 2.76, 2.60 and 10.03 ppm, respectively. The N–H signal disappeared both on deuteration or complex formation. The chemical shifts of both Me–C=N and MeS- are more or less the same as those observed in the spectra of *N*-isopropylidene hydrazine-*S*-methyl carbodithioate (*3*, R$_1$, R$_2$ = Me)$^{(23)}$. This indicates that the Me–C=N group in Dahydth is not affected by the anisotropy of the acetyl group and most probably exists in *s-cisoid* configuration. The ^{1}H n.m.r. spectra of the corresponding zinc(II) and cadmium(II) chelates, show the Me–C=N signal at much lower fields (δ *ca.* 2.50 ppm) as compared to the spectrum of Dahydth. Such a deshielding effect may suggest a *s-transoid* configuration for the deprotonated ligand in these chelates, where the Me–C=N group lies within the deshielding cone of the acetyl carbonyl group. Pseudo-aromatic character proposed for such a chelate ring may also contribute$^{(24–26)}$, but to a less extent to the observed deshielding effect.

The SMe protons in the ^{1}H n.m.r. spectra of Benhydth, appear as two resolved signals (J = 1.95 Hz) and the intensity ratio of the high to low field signals decreases with temperature. This behaviour indicates that the SMe group must exist in two different environments, which can be related to the partially restricted rotation around the NH-CSSMe bond in a polymeric, or at least dimeric, structure$^{(27)}$. The SMe group in this aggregate can attain either a *cis* or *trans* configuration with respect to the N–N bond. Increasing the temperature will favour the *trans* configuration *(10a)*, where the SMe protons of one molecule are in the deshielding field of the phenyl group of the other. In the *cis* configuration however, the SMe protons are far away from the phenyl field effects *(10b)*.

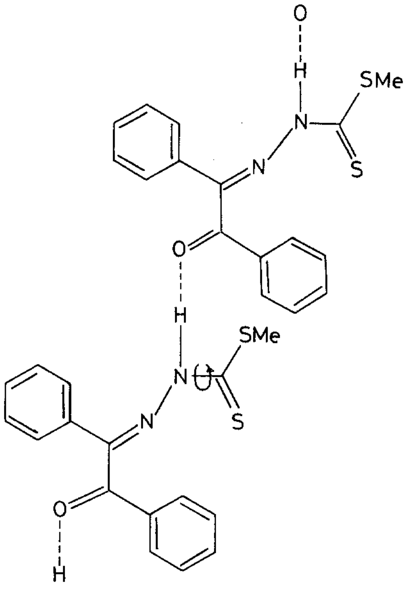
In diamagnetic bis-ligand chelates, M(Benhydth-H)$_2$ [M = zinc(II), cadmium(II), nickel(II) and palladium(II)] the SMe protons appear as a singlet at relatively high field as compared with M(Dahydth-H)$_2$ [M = zinc(II), and cadmium(II)] chelates. This shielding effect suggests that the SMe protons in M(Benhydth-H)$_2$ are located in the phenyl shielding cone. This can be achieved, as proved from a study of molecular models, in a distorted stepped or tetrahedral structure.

The mass spectra of both Dahydth and Benhydth as well as their corresponding bis-ligand metal(II) chelates were also determined and the relative intensities of the major ions are listed in Tables 5 and 6 respectively, the proposed mechanism for the fragmentation of the ligand molecules is given in Scheme 2. Only the spectrum of Dahydth displays the molecular ion (m/e = 190). The largest fragment in the spectrum of Benhydth, however corresponds to the ligand-MeSH ion (m/e = 267) which is formed by the rearrangement of the molecular ion to the thiol form and subsequent loss of a neutral MeSH

Table 4. ^{1}H n.m.r. spectra of Dahydth, Benhydth and their metal(II) chelates

Compound	δ (ppm) Me–C=N	Me–C=O	SMe	Ph–C=N	Ph–C=O	N–H
Dahydth	2.16	2.60	2.76	–	–	10.03[a]
$Zn(Dahydth\text{-}H)_2$	2.50	2.55	2.61	–	–	–
$Cd(Dahydth\text{-}H)_2$	2.50	2.58	2.68	–	–	–
Benhydth	–	–	2.80d[b]	7.33–7.83(m)	8.16–8.36(m)	10.10[a]
$Zn(Benhydth\text{-}H)_2$	–	–	1.86	7.33–7.53(m)	7.60–7.80(m)	–
$Cd(Benhydth\text{-}H)_2$	–	–	1.93	7.40–7.86(m)		–
$Ni(Benhydth\text{-}H)_2$	–	–	1.97	7.33–7.63(m)	8.76–9.00(m)	–
$Pd(Benhydth\text{-}H)_2$	–	–	2.00	7.33–7.86(m)	8.00–8.23(m)	–

[a] Exchangeable with D_2O; [b] J = 1.95 Hz.



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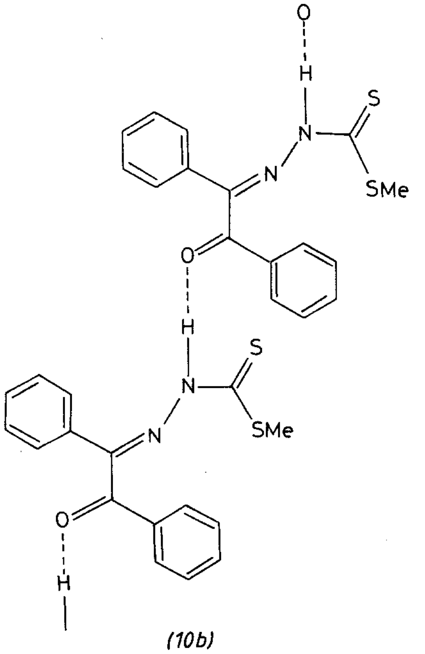

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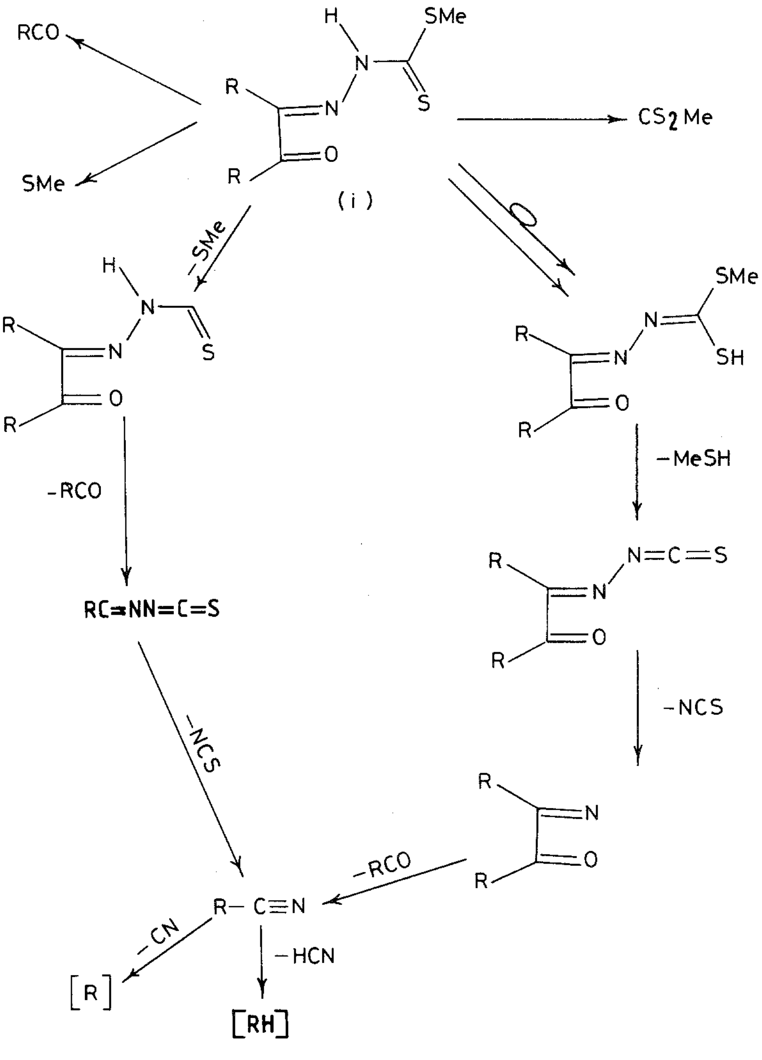


Scheme (2).

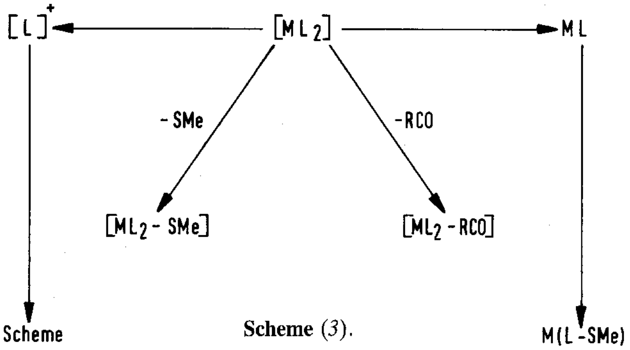
molecule. A similar mechanism was proposed previously by Das and Livingstone[19] for the fragmentation of bidentate hydrazine-*S*-methylcarbodithioate Schiff bases. The spectra of both Dahydth and Benhydth also show ions corresponding to ligand-RCO, ligand-CSSMe, RCO and CSSMe fragments.

The fragmentation patterns of bis-ligand metal(II) chelates depend on the nature of the metal ion as well as the nature of R. Only the spectrum of $Ni(Dahydth\text{-}H)_2$ shows the molecular ion NiL_2 (m/e = 439), besides NiL_2-2MeCO and NiL; while

Table 5. Mass spectra of Dahydth and Benhydth ligands of the general formula $R(RCo)NNHCS_2Me$

Fragment	Relative abundance (%) R = Me	R = Ph
L[a)]	16.86	–
L-SMe	–	9.32
L-COR	72.82	87.88
$L-CS_2Me$	7.02	–
L-COR-SMe	–	10.13
CS_2Me	22.75	7.99
SMe	10.89	12.96
COR	100.00	100.00
RC=N	3.86	16.39
R	–	96.22

[a)] L = Ligand.



Scheme (*3*).

the spectrum of $Zn(Dahydth\text{-}H)_2$ displays peaks due to ZnL_2-MeCO and ZnL. The corresponding cadmium(II) and copper(II) chelates, however, do not show any ligand fragment containing metal ion. All the spectra show the ligand ion and other ligand fragments similar to that given in Scheme 3.

The $M(Benhydth\text{-}H)_2$ chelates, on the other hand, show different behaviour in the mass spectrometer. The spectra, in general are very complicated by a larger number of metastable ions. The $Ni(Benhydth\text{-}H)_2$ similar to the corresponding copper(II) and cadmium(II) chelates do not show any ligand fragment containing metal ion, but show ions due to ligand fragmentation. The spectrum of $Zn(Benhydth\text{-}H)_2$, however, displays ions corresponding to ZnL_2-SMe, ZnL_2-PhCO, ZnL and ZnL-SMe.

Experimental

Organic ligands

Monohydrazine-S-methylcarbodithioate Schiff bases (6, R_1, R_2 = Me; R_1, R_2 = Ph)

A solution of hydrazine-*S*-methylcarbodithioate (0.1 mole) in absolute EtOH [30 cm^3 was added to a solution of the diketone (0.1 mole) in absolute EtOH (30 cm^3)]. The reaction mixture was boiled under reflux for 30 min and then concentrated by evaporation to half its vol. On cooling, the precipitate (R_1, R_2 = Me; or R_1, R_2 = Ph) was filtered off and recrystallized from absolute EtOH (M.p. *(6)*, R_1, R_2 = Me, 152 °C and R_1, R_2 = Ph, 104°).

Metal (II) chelates

M(α-dikhydth-H)$_2$ chelates (M = $Zn^{(II)}$, Cd^{II}, Cu^{II} or Ni^{II})

A solution of the metal(II) acetate (0.01 mole) in EtOH (30 cm^3) was added to a solution of the Schiff base (*6*, R_1, R_2 = Me; R_1, R_2 = Ph) (0.02 mole) in absolute ethanol (40 cm^3). The reaction mixture was boiled under reflux for 1 h and left to cool. The neutral metal(II) bis chelates, which separated out, were filtered, washed with EtOH, and recrystallized from $CHCl_3$: light petroleum.

Pd(Benhydth-H)$_2$ chelate

A hot solution of $Na_2[PdCl_4]$ (0.01 mole) in EtOH was added to a hot solution of Benhydth (0.02 mole) in EtOH (30 cm^3) and the mixture was boiled under reflux for 2 h. The resulting $Pd(Benhydth\text{-}H)_2$ was filtered while hot and dried *in vacuo* over $CaCl_2$.

Physical measurements

Magnetic, i.r., electronic and ^1H n.m.r. spectral data were recorded using the same procedures described previously$^{(28)}$. The mass spectra were measured using an AEI MS902 mass spectrometer.

Table 6. Characteristic fragments in the mass spectra of α-diketone monohydrazone-*S*-methylcarbodithioate metal(II) chelates

Fragment	Relative abundance (%) R_1, R_2 = Me Ni	Zn	Cu	Cd	R_1, R_2 = Ph Ni	Cu	Zn	Cd
ML_2[a)]	1.83	–	–	–	–	–	–	–
ML_2-SMe	–	–	–	–	–	–	4.29	–
ML_2-RCO	1.52	2.33	–	–	–	–	81.85	–
ML	8.52	8.27	–	–	–	–	99.47	–
L	7.15	–	1.65	–	–	–	8.90	–
L-SMe	27.07	47.63	28.70	46.24	–	–	100.00	44.25
L-RCO	37.28	33.50	47.63	13.86	2.11	1.47	11.70	–
CS_2Me	21.21	100.00	36.70	98.33	1.95	1.09	12.49	9.18
SMe	45.73	100.00	100.00	100.00	4.96	1.14	26.00	15.60
RCO	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
RC=N	32.17	68.47	100.00	38.76	11.68	–	100.00	98.20
R	–	–	–	–	97.79	100.00	100.00	100.00
$L-CS_2Me$	29.60	51.51	100.00	43.74	–	–	–	–

[a)] L = Ligand.

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Reactions of $[MCl_6]^{2-}$ (M = Tc or Re) with Salicylaldehyde. The Molecular Structure of Tetraphenylphosphonium Tetrachloro(salicylaldehydato) technetate (IV)

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Summary

The $[PPh_4][TcCl_4(sal)]$ and $[PPh_4][ReOCl_3(sal)]$ (sal = o-OC_6H_4CHO) complexes were synthesized from $[PPh_4]_2[MCl_6]$ (M = Tc or Re) and salicylaldehyde. The complexes were characterized by elemental analysis, magnetic susceptibility and conductivity measurements and i.r. spectrometry. The structure of $[PPh_4][TcCl_4(sal)]$ was determined by x-ray methods and consists of well-separated units of octahedral $[TcCl_4(sal)]^-$ anions and tetrahedral $[PPh_4]^+$ cations. The equatorial plane of the octahedron is formed by two Cl atoms and the chelated $\overset{\frown}{O(1)O(2)}$ sal group, with the resulting $TcCl_2$(sal) unit approximately planar. Selected values in the anion are as follows: Tc–Cl(mean) 2.34(1), Tc–O(1) 2.04(2) and Tc–O(2) 1.98(2), O(1)- - -O(2)('byte') 2.83 Å; O(1)–Tc–O(2) 89.3(0.7)°.

Introduction

A recent route to produce new and more efficacious ^{99m}Tc radiopharmaceuticals involves the use of prereduced complexes of technetium. The most frequently studied technetium reduced complexes are $[TcOCl_4]^-$ (1–4), $[TcX_6]^{2-}$ (5, 6) (X = Cl or Br) and Tc^V(gluconate)(7).

The present work is concerned with reactivity studies of $[TcCl_6]^{2-}$ with salicylaldehyde in the attempt to explore the possibility of producing technetium(IV) complexes with chelating ligands of the type $\overset{\frown}{O\ O}$ characteristic of many biological systems to be potentially labelled with ^{99m}Tc. With the aim of making comparative studies of rhenium and technetium, we have investigated the reactivity of $[ReCl_6]^{2-}$ under the same experimental conditions. The complexes were studied and characterized by elemental analysis, conductivity and magnetic susceptibility measurements in solution, by i.r. spectroscopy and by x-ray analysis.

Experimental

Materials and apparatus

Solutions of $[TcO_4]^-$ in 0.1 M NH_4OH were purchased from the Radiochemical Centre, Ltd. Amersham (England) and concentrated to obtain solid samples. The preparations of $[TcCl_6]^{2-}$ and $[ReCl_6]^{2-}$ were achieved using methods reported elsewhere(8, 9). The $[PPh_4]_2[MCl_6]$ complexes were synthesized by treating the $[MCl_6]^{2-}$ solutions with Ph_4PCl in H_2O.

Other materials were commercially available reagent grade chemicals. Elemental analyses of technetium, phosphorus and chlorine were performed as reported elsewhere(10). I.r. spectra of samples in nujol mulls between CsI discs or in KBr pellets were collected on a Perkin-Elmer 580B spectrophotometer.

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