Figure 3. Configuration of the complex [ReCl(CO)(PMe₂Ph)₃-(MeCN)₂][ClO₄]₂.

reduction peak, resulting in any case in the consumption of two moles of electrons per mole of starting compound. The electrolyzed solutions were concentrated to dryness and the product collected. In the case of the triphenylphosphine complex, the dried mixture was washed with CHCl₃, yielding a yellow solution which, by addition of n-pentane, gave a pale yellow powder. By washing with H₂O, the residual TEAP was separated from the powder, which was dried under vacuum. Final recrystallization was performed from CHCl₃ and Et₂O. In the case of the dimethylphenylphosphine complex, the same products were obtained from both *meridional* and *facial* isomers. The solution turned after some hours from bright yellow to yellow green. After drying, the mixture was washed with Et₂O to remove the free phosphine and then with CHCl₃. The CHCl₃ solution was concentrated to dryness and the residual solid was treated with MeCN. By dropping Et₂O into the solution, TEAP precipitated. After filtration, Et₂O was added again, until a pale yellow oil was obtained. The oil was stirred in Et₂O for hours to obtain a white powder. Recrystallization was performed from CHCl₃ and Et₂O. Reproducible elemental analysis data were obtained for the product with

PPh₃: C, 53.5; H, 5.2; N, 1.4 and Cl, 0.0%. They are consistent with a formulation in which there are two moles of phosphine and one tetraethylammonium per rhenium.

I.r. spectra show in the $\nu(CO)$ region bands at 1897, 1807 cm^{-1} and at 1890, 1802 cm^{-1} for PPh₃ and PMe₂Ph compounds, respectively. The ¹H n.m.r. spectra in CDCl₃ show a triplet at δ = 1.3 ppm and a quartet at δ = 2.4 ppm, typical of the tetraethylammonium cation and the multiplet of phenyl ring at δ = 7.7 ppm. The compound with PMe₂Ph shows an additional triplet at δ = 1.9 ppm, which is attributable to the methyl protons of the phosphine and suggests *trans*-phosphines. Both compounds conduct in nitromethane solutions.

Unfortunately, the above data do not provide a sure formulation of the reduction compounds. The number of carbonyl groups and the molecular weight are unclear. The rhenium is reduced and stabilized in the −I oxidation state, the complex is anionic and it could have bridging carbonyls. The formulation can be tentatively written as [Et₄N][{Re(CO)ₓP₂}ₙ], with x = 2 or 3 and n = 1 or 2. Further studies are in progress to characterize the complexes.

References

[1] P. M. Treichel, *J. Organomet. Chem.*, **242**, 205 (1983) and refs. therein. – [2] F. Calderazzo, F. Marchetti, R. Poli, D. Vitali, P. F. Zanassi, *Chem. Comm.*, 893 (1981). – [3] F. Calderazzo, F. Marchetti, R. Poli, D. Vitali, P. F. Zanassi, *J. Chem. Soc., Dalton Trans.*, 1665 (1982). – [4] R. Seeber, G. A. Mazzocchin, E. Roncari, U. Mazzi, *Transition Met. Chem.*, **6**, 123 (1981). – [5] E. Roncari, U. Mazzi, R. Seeber, P. Zanello, *J. Electroanal. Chem.*, **132**, 221 (1982). – [6] G. A. Mazzocchin, R. Seeber, U. Mazzi, E. Roncari, *Inorg. Chim. Acta, 29*, 1 (1978). – [7] G. A. Mazzocchin, R. Seeber, U. Mazzi, E. Roncari, *Inorg. Chim. Acta, 29*, 5 (1978). – [8] U. Mazzi, E. Roncari, R. Seeber, G. A. Mazzocchin, *Inorg. Chim. Acta, 41*, 95 (1980). – [9] P. G. Douglas, B. L. Shaw, *J. Chem. Soc. A*, 1491 (1969). – [10] J. Chatt, J. R. Dilworth, H. P. Gunz, G. J. Leigh, *J. Organomet. Chem., 64*, 245 (1974).

[11] D. F. Evans, *J. Chem. Soc.*, 2003 (1959). – [12] G. Bandoli, D. A. Clemente, U. Mazzi, *J. Chem. Soc., Dalton Trans.*, 373 (1978). – [13] R. S. Nicholson, *Anal. Chem., 37*, 1351 (1965).

Complexes of Divalent Nickel and Copper with the Schiff Base Derived from 2-(2-Aminophenyl)benzimidazole and Benzaldehyde

Pilar Souza, José A. García-Vázquez* and José R. Masaguer

Departamento de Química Inorgánica. Universidad Autónoma. Cantoblanco Madrid-34, Spain

Summary

The reactions of divalent nickel and copper salts with the Schiff base derived from 2-(2-aminophenyl)benzimidazole and

benzaldehyde, L, yield complexes of general formulae [CuL₂X₂] (X = Cl, Br, or ClO₄), [CuL(SO₄)], [CuL(SO₄)] · 4H₂O, and NiLX₂ (X = Cl, Br, or NCS).

All the complexes have been characterized by elemental analyses, magnetic measurements, e.s.r. electronic and i.r.

* Author to whom all correspondence should be addressed.

spectral studies. The results show that the Schiff base acts as bidentate ligand through the pyridine-like imine nitrogen of imidazole ring and the azomethine nitrogen. Tentative structures of the complexes are suggested.

Introduction

Imidazole is a common component of some important biological molecules[1, 8] and together with its derivatives has been the subject of several investigations[1–7]. Normally, when the substitution is not in the position 1 of the imidazole ring, the imidazoles act as monodentate ligands coordinating through the tertiary nitrogen, but sometimes the N–H is also deprotonated to form a bidentate bridge[9]. Comparatively little work have been reported on complexes of ligands that contain the imidazole group and another potential donor group[10, 11].

The present study describes coordination complexes formed by the interaction of some copper and nickel salts with the Schiff base derived from 2-(2-aminophenyl)benzimidazole and benzaldehyde. The structure and the nature of the complexes were investigated by magnetic susceptibility, i.r. electronic absorption and e.s.r. measurements.
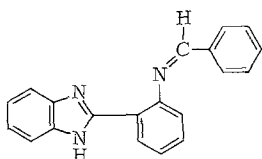
Experimental

Solvents and benzaldehyde were purifed and dried according to standard methods. 2-(2-Aminophenyl)benzimidazole was recrystallized from 1,2-dichloroethane. Nickel thiocyanate was prepared by addition of KNCS to an EtOH solution of $Ni(NO_3)_2 \cdot 6H_2O$ with mechanical stirring for 3 h. The precipitate of KNO_3 was removed by filtration. Commercial reagent grade nickel and copper anhydrous salts were used (with the exception of the preparation of $CuLSO_4 \cdot 4H_2O$ and $CuLClO_4$ which were prepared from the hydrated salts).

The Schiff base was prepared by heating in benzene under reflux equimolecular amounts of the 2-(2-aminophenyl)benzimidazole and benzaldehyde, with some drops of piperidine, until the theoretical amount of water was collected in a Dean-Stark trap. The isolated solid was washed with C_6H_6 and Et_2O. (Found: C, 80.6; H, 5.0; N, 14.1. Calcd.: C, 80.8; H, 5.1; N, 14.1%).

Preparation of complexes

All preparations and sampling were made in a dry-box which was continuously flushed with dry nitrogen.

A general procedure was adopted for preparing all the complexes. A solution of the Schiff base (5.1 mmole) in EtOH (30 cm^3) was added dropwise to a hot solution of the appropriate metal salt (2.9 mmole) in the same solvent (25 cm^3) under continuous stirring. The mixture was kept stirring under reflux for about 10–20 h. The precipitate was filtered off, washed with EtOH and dried *in vacuo* at room temperature.

Metal analyses were carried out by absorption spectrophotometry on a Perkin Elmer-372 spectrometer after decomposing the complexes with a mixture of nitric and sul-phuric acids. C, H and N contents were determined using standard microanalytical techniques.

Physical measurements

Conductivity measurements were made on freshly prepared *ca.* 10^{-3} M solutions in DMF at 20 °C with a Metrohm Herisau model E-518. Magnetic susceptibilities were measured at room temperature by the Faraday method with a BE 15 Bruker balance. $Hg[Co(NCS)_4]$ was used as the magnetic susceptibility standard. Pascal's constants were used for the diamagnetic corrections[12]. Magnetic moments were calculated using the equation $\mu_{eff} = 2.83 \sqrt{\chi_M^{corr} T}$. The solid reflectance spectra were obtained in a Beckman DK-2 spectrophotometer with a solid reflectance attachment, using magnesium oxide as the reference. The solution spectra were recorded on a Pye Unicam SP8-100 spectrophotometer. I.r. spectra were recorded as Nujol or hexachlorobutadiene mulls between CsI plates on a Nicolet 5 DX spectrophotometer. The e.s.r. spectra were recorded on a Varian E-12 spectrometer at a microwave frequency of 9 GHz (X-band) using DPPH for calibration. The low-temperature spectra were recorded in a variable temperature cell.

Results and Discussion

The complexes isolated in the present study and their analytical data are given in Table 1. The compounds prepared are insoluble in most of the common organic solvents. The copper complexes are soluble in DMF. The copper complexes are non-conductors in *ca.* 10^{-3} M solutions in DMF[13].

Infrared spectra

The i.r. spectra of the complexes reveal that most bands due to ligand vibrations are scarcely shifted with respect to the corresponding free ligand values. Only the N–H and C = N stretching vibrations show a large shift. The $\nu(NH)$ of ligand at *ca.* 3330 cm^{-1} is shifted to lower frequency (10–45 cm^{-1}) in all complexes. This shift may be due to stronger hydrogen bonding between the ligand and the anions[4, 14] in complexes than the intermolecular hydrogen bonding in the ligand in the solid state[15, 16]. The medium intensity band at *ca.* 1615 cm^{-1} in the ligand attributable to $\nu(C = N)$ is found in the region 1620–1636 cm^{-1} in the complexes, indicating that the imine nitrogen of the C = N group participates in coordination[17, 18].

On the other hand, the bands at 289 cm^{-1} in $[CuL_2Cl_2]$ and at 219 cm^{-1} in CuL_2Br_2 can be assigned to terminal $\nu(Cu–Cl)$ and $\nu(Cu–Br)$, respectively, in hexa-coordinated octahedral structures[19, 20]. The spectra of $NiLCl_2$ do not contain any band assignable to terminal $\nu(Ni–Cl)$ and this is in agreement with a polymeric octahedral structure. The bridging $\nu(Ni–Cl)$ modes are expected to absorb below 200 cm^{-1} [21, 22], which is beyond the capabilities of our spectrometer. The spectra of $NiLBr_2$ show a band at 208 cm^{-1}, which is assigned to a terminal $\nu(Ni–Br)$ in a five-coordinate structure[23]. The bridging $\nu(Ni–Br)$ expected below 200 cm^{-1} could not be observed.

The spectra of perchlorate complex show various bands at *ca.* 1095, 1076, 931, 622 and 628 cm^{-1} consistent with the monodentate nature of perchlorate group[21, 24]. The spectra of $CuLSO_4$ show new bands at *ca.* 1190, 1093, 1042, 975, 636, 613 and 606 cm^{-1}, which are characteristic of the bidentate sulphate group[25]. In the spectra of $[CuL_2SO_4] \cdot 4H_2O$, new bands at *ca.* 1118, 1048, 976, 654 and 588 cm^{-1}, which are

Table 1. Analytical data of nickel(II) and copper(II) complexes.

Compound	Colour	Λ_M (Ohm^{-1}cm^{2}mol^{-1})	Found (Calcd.) %			
			C	H	N	M
NiLCl$_2$	green		56.1(56.2)	3.7(3.5)	10.2(9.8)	13.3(13.8)
NiLBr$_2$	pale green		47.0(46.5)	3.3(2.9)	8.3(8.1)	11.2(11.4)
NiL(NCS)$_2$	pale green		55.6(55.9)	3.5(3.2)	14.4(14.8)	12.1(12.4)
[CuL$_2$Cl$_2$]	green	8.5	65.7(65.9)	4.5(4.1)	10.8(11.5)	8.4(8.7)
[CuL$_2$Br$_2$]	green brown	22	58.8(58.7)	3.2(3.7)	10.6(10.3)	7.7(7.8)
[CuL$_2$(ClO$_4$)$_2$]	brown	19	55.9(56.1)	3.8(3.5)	10.0(9.8)	7.2(7.4)
[CuLSO$_4$]	green	12	51.8(52.6)	3.1(3.3)	9.0(9.2)	13.5(13.9)
[CuLSO$_4$] · 4 H$_2$O	light green	13.1	43.7(43.9)	4.5(4.6)	7.6(7.7)	11.6(11.6)

consistent with a monodentate sulphato group[26]. This compound also shows bands at ca. 3450 and 758 cm^{-1}, which can be assigned to ν(OH) and rocking modes of coordinated water in this compound[27]. The spectra of the thiocyanate complex show additional bands at ca. 2102, 800, 469 and 445 cm^{-1}, suggesting the presence of an N-bonded[28] or bridged[29, 30] thiocyanate group, but we favour the latter in view of the electronic spectra.

Some new bands appear in the i.r. spectra of all the complexes at ca. 420–520 cm^{-1}. The bands at ca. 450–490 cm^{-1} in copper and 430–450 cm^{-1} in nickel complexes may tentatively be assigned to ν(Cu–N) and ν(Ni–N) (imine nitrogen), respectively[31, 32]. The appearence of bands in the 300–310 cm^{-1} and the 255–270 cm^{-1} regions for all the Cu and Ni complexes, respectively, can tentatively be assigned to ν(M–N) (pyridine-like imine nitrogen)[33], and also supports the involvement of this nitrogen. Therefore, these data indicate that the ligand is bidentate in these complexes.

Magnetic moments and electronic spectra

The magnetic moments of the nickel(II) complexes lie in the region of 2.5–2.8 B.M. at room temperature (Table 2). These values are lower than the expected for high spin d^8 complexes and higher than those predicted for low spin N^{II} complexes, even taken into account the TIP contribution. These anomalous values of the magnetic moments may be due either to a coexistence of low and high spin species[35, 36] or to a spin-state crossover situation where high and low states are simultaneously thermally populated[5, 35].

The electronic reflectance spectra (Table 2) of NiL(NCS)$_2$ and NiLCl$_2$ show two bands at ca. 10000 and 17000 cm^{-1} with a well discernable shoulder at ca. 9000 cm^{-1} on the low energy side of the first band. The spectral bands are well within the range for hexacoordinate octahedral complexes of nickel

reported earlier[36]. The two bands can be assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(\nu_2)$ transitions, respectively. The shoulder may be due to the splitting of ν_1 as a consequence of the distorted octahedral nature of the complexes[37]. Although the electronic spectra of these complexes suggest that nickel is hexacoordinate, the possibility that the ca. 17000 cm^{-1} band be a result of the $^3A_{2g} \rightarrow {}^3T_{1g}$ transition in octahedral structure and of the $^1A_1(F) \rightarrow {}^1B_1(G)$ in square planar structure[35] cannot be ruled out. Therefore, the possible structures for these complexes are: (a) polymeric octahedral with chloride or thiocyanate bridges, with a singlet-triplet equilibrium or (b) polymeric with chloride of thiocyanate bridges, in which a part of the nickel ions are octahedrally coordinated (high spin), whereas the other are planar (low spin).

The electronic spectra of NiLBr$_2$ are different to those of NiLCl$_2$ and NiL(NCS)$_2$, showing three bands at ca. 7900, 12578 and 17094 cm^{-1}. The spectral bands are not consistent with those reported for tetra- or hexa-coordinated structures[36, 37], but they resemble those of nickel pentacoordinated complexes[38, 39]. It is suggested therefore that NiLBr$_2$ is probably dimeric pentacoordinate, with bromide bridges and its magnetic moment may be explained assuming that the complex consists of species with low and high spin type or that there is a single-triplet equilibrium.

The magnetic moments of the copper(II) complexes lie in the region of 1.8–2.1 B.M., very close to the spin only values.

The solid reflectance and DMF solution electronic spectra for all the copper(II) complexes (Table 2) are approximately the same, suggesting that these complexes probably retain the same structures in both states. The only exception is CuL(SO$_4$), which shows a bathochromic shift in the d–d maxima. The solid spectrum of [CuLSO$_4$], exhibits an asymmetric band at 17500 cm^{-1}, similar to that reported for a copper(II) ion in a square planar environment[36]. The shift observed in solution is assumed to be due to weak axial bonding of solvent

Table 2. Magnetic and electronic data for nickel(II) and copper(II) complexes and powder e.s.r. data for copper(II) complexes.

Compound	μ_{eff} (B.M.)	Spectral bands (cm^{-1}) Solid spectra	Solution spectra	E.s.r. data			
NiLCl$_2$	2.53	9090sh, 9800, 16130	–	–			
NiLBr$_2$	2.72	7900, 12580, 17540	–	–			
NiL(NCS)$_2$	2.78	8710sh, 10700, 17860	–	–			
[CuL$_2$Cl$_2$]	1.88	13790, 18870	13700, 18820	2.068			
[CuL$_2$Br$_2$]	1.97	13850, 19180	13810, 19200	2.118			
[CuL$_2$(ClO$_4$)$_2$]	1.89	14330	14300	2.065			
				g_1	g_2	g_3	g_{av}
[CuLSO$_4$]	2.07	17240	13510	2.050	2.095	2.277	2.141
[CuLSO$_4$] · 4 H$_2$O	2.19	14660	14630	2.048	2.088	2.269	2.135

Table 3. Solution (DMF) e.s.r. data and covalency parameters for the copper(II) complexes.

Compound	Room temp.		93 K						
	g_0	$10^4 A_0$ (cm^{-1})	$g_\parallel$	$g_\perp$	g_{av}	$10^4 A$ (cm^{-1})	α^2	β_1^2	β^2
$[CuL_2Cl_2]$	2.156	49	2.320	2.063	2.148	134	0.75	0.88	0.67
$[CuL_2Br_2]$	2.160	51	2.297	2.078	2.151	141	0.76	0.81	0.83
$[CuL_2(ClO_4)_2]$	2.154	70	2.269	2.080	2.144	169	0.81	0.71	0.83
$[CuLSO_4] \cdot 4\,H_2O$	2.137	61	2.251	2.073	2.132	173	0.80	0.69	0.78

molecules resulting in a decrease in the planar bonding[40]. The electronic spectra of the other copper complexes show a broad band in the 13000–15000 cm^{-1} range. The general features of these spectra are consistent with distorted octahedral structures. This band in $[CuL_2X_2]$ (X = Cl, Br, or ClO_4) shifts to higher energy in the order of expected weakening interaction of the metal ion with the anions: $ClO_4 > Br > Cl$. A second stronger band appears at ca. 18000 cm^{-1} for $[CuL_2Cl_2]$ and $[CuL_2Br_2]$, and can be assigned to a charge-transfer transition[41].

E.s.r. spectra

The e.s.r. spectra of $[CuL_2Cl_2]$, $[CuL_2Br_2]$ and $[CuL_2(ClO_4)_2]$ powdered complexes show one single asymmetric signal. The only parameter than can be calculated from this spectra is g_{max} at the point where the value of the derivative is zero. The other complexes give rise to typical orthorhombic spectra with three g values similar to those described in the literature[42]. The existence of orthorhombic symmetry is probably due to the presence of two crystallographically non-equivalent molecules[43].

The e.s.r. spectra in DMF (Table 3) at room temperature consist of the usual four hyperfine lines. The spectra at liquid nitrogen temperature are of the axial type ($g_\parallel > g_\perp$) and are consistent with a ground state which is primarily $d_{x^2-y^2}$ for species having a tetragonal structure[42]. It has been found[44] for this structure type that the stronger the axial ligand coordination, the lower is the A value and the higher the g (where there are equivalent equatorial ligands). Therefore, the values A and g for $[CuL_2X_2]$ (X = Cl, Br, or ClO_4) suggest that the strength of the axial ligand coordination decreases in the sequence Cl > Br > ClO_4, which is in agreement with the order found from the electronic spectra. Table 3 shows the covalency parameter calculated[45, 46] from the data derived from DMF solution experiments. The values found for α^2 indicate moderate covalency for the σ-bonding and they are in the range expected for the copper complexes with tetragonal distortion: 0.83–0.84 nitrogen donor ligands[47] and 0.84–0.9 oxygen donor ligands[48]. The β^2 and β_1^2 values indicate a significant covalency in the π-bond in- and out-of-the-plane, respectively[46].

References

[1] R. J. Sundberg and R. B. Martin, *Chem. Rev.*, 74, 471 (1974) and refs. therein. – [2] J. A. Welleman, F. B. Hulsbergen, J. Verbiest and J. Reedijk, *J. Inorg. Nucl. Chem.*, 40, 143 (1978). – [3] F. Mani and G. Scapacci, *Inorg. Chim. Acta*, 16, 163 (1976). – [4] F. Mani, *Inorg. Nucl. Chem. Lett.*, 12, 271 (1976). – [5] P. Pujari and K. C. Dash, *J. Inorg. Nucl. Chem.*, 38, 1891 (1976) and refs. therein. – [6] A. Mishra and J. P. Singh, *J. Inorg. Nucl. Chem.*, 41, 905 (1979). – [7] J. B.

Hodgson, G. C. Percy and D. A. Thornton, *J. Mol. Struct.*, 66, 81 (1980). – [8] M. N. Hughes, *The Inorganic Chemistry of Biological Process*, Wiley, London, 1972. – [9] E. M. Bridson and R. M. Walker, *Aust. J. Chem.*, 23, 1973 (1970). – [10] M. J. M. Campbell, D. M. Card and R. Grzeskowiak, *J. Chem. Soc., Dalton Trans.*, 1687 (1972).

[11] M. J. M. Campbell, R. Grzeskowiak and S. G. Juneja, *J. Inorg. Nucl. Chem.*, 36, 2485 (1974). – [12] B. N. Figgis and J. Lewis in J. Lewis and R. G. Wilkins (Eds.), *Modern Coordination Chemistry*, Interscience, New York, 1968. – [13] W. J. Weary, *Coord. Chem. Rev.*, 7, 81 (1971). – [14] J. Reedijk, *Rec. Trav., Chim.*, 88, 1451 (1969). – [15] J. B. Hodgson, G. C. Percy and D. A. Thornton, *J. Mol. Struct.*, 66, 75 (1980). – [16] M. Soares, *Rev. Port. Quim.*, 6, 112 (1964). – [17] M. N. Patel, C. B. Patel and R. P. Patel, *J. Inorg. Nucl. Chem.*, 36, 3868 (1974). – [18] M. R. Mahmoud and M. T. El-Haty, *J. Inorg. Nucl. Chem.*, 42, 349 (1980). – [19] R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, 4, 350 (1965). – [20] J. R. Ferraro, *Low Frequency Vibrations of Inorganic and Coordination Compounds*, Plenum Press, New York, 1971.

[21] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley, New York, 1970. – [22] A. Giusti and G. Peyronel, *Transition Met. Chem.*, 4, 35 (1979). – [23] M. Keeton and B. P. Lewer, *Inorg. Chem.*, 10, 47 (1971). – [24] M. Milkuski, L. L. Pytlewski and N. M. Karayannis, *Synth. React. Inorg. Met. Org. Chem.*, 9, 401 (1979). – [25] G. C. Barraclough and M. L. Tobe, *J. Chem. Soc.*, 2276 (1960). – [26] M. P. Teotia, J. N. Gurtu and V. B. Rana, *J. Inorg. Nucl. Chem.*, 42, 821 (1980). – [27] R. A. Bailey, S. L. Kozak, T. W. Michelsen and W. N. Mills, *Coord. Chem. Rev.*, 6, 407 (1970). – [28] I. S. Ahuja, R. Singh and R. Sriramulu, *Transition Met. Chem.*, 3, 185 (1978). – [29] M. V. Artemenko, E. A. Chistyakova, P. A. Suprunenko and G. I. Kal'naya, *Russ. J. Inorg. Chem.*, 16, 1026 (1971). – [30] V. B. Rana, D. P. Singh, P. Singh and M. P. Teotia, *Transition Met. Chem.*, 6, 60 (1981).

[31] V. B. Rana, D. P. Singh, P. Singh and M. P. Teotia, *Transition Met. Chem.*, 6, 36 (1981) and refs. therein. – [32] B. C. Cornilsen and K. Nakamoto, *J. Inorg. Nucl. Chem.*, 36, 2467 (1974). – [33] D. A. Baldwin, A. B. P. Lever and R. V. Parish, *Inorg. Chem.*, 8, 107 (1969). – [34] G. M. Mockler, G. M. Chaffey, E. Sinn and H. Wong, *Inorg. Chem.*, 11, 1308 (1972) and refs. therein. – [35] M. Shaefer and E. Uhlig, *Z. anorg. allg. chem.*, 407, 23 (1974). – [36] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1968. – [37] D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 6, 1092 (1967). – [38] L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, 88, 5180 (1966). – [39] M. Mohan and M. Kumar, *Synth. React. Inorg. Met-Org. Chem.*, 13, 639 (1983). – [40] D. R. McMillin, R. S. Drago and J. S. Musz, *J. Am. Chem. Soc.*, 98, 3120 (1976).

[41] D. X. West and W.-H. Wang, *J. Inorg. Nucl. Chem.*, 43, 1511 (1981). – [42] B. J. Mathaway and D. E. Billing, *Coord. Chem. Rev.*, 5, 143 (1970). – [43] J. Kohout, M. Quastlerova-Hvastijova and J. Gazo, *Inorg. Chim. Acta*, 8, 21 (1974). – [44] M. Massacesi, G. Ponticelli, C. Ramachary and V. G. Krishman, *Transition Met. Chem.*, 5, 353 (1980). – [45] P. Kivelson and R. Neiman, *J. Chem. Phys.*, 35, 149 (1961). – [46] H. Henning and R. Kirmse, *Z. anorg. allg. chem.*, 388, 238 (1972). – [47] D. R. Lorenz, J. R. Jasson, P. R. Johson and D. A. Thorpe, *J. Inorg. Nucl. Chem.*, 37, 2297 (1975). – [48] D. R. Johson, H. J. Stoklosa, J. R. Wasson and G. L. Seebach, *J. Inorg. Nucl. Chem.*, 37, 1397 (1975).