Oxo-tricyano complexes of molybdenum(IV) and tungsten(IV) with bidentate Schiff bases

Beata Burda*, John Burgess† and Simon A. Parsons

Department of Chemistry, Leicester University, University Road, Leicester LE1 7RH, UK

Alina Samotus† and Janusz Szklarzewicz

Faculty of Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Kraków, Poland

Summary

The reaction of $[M(CN)_4O(OH_2)]^{2-}$ (M = Mo or W) with 2-acetylpyridine and methyl- or butyl-amine in a water–MeOH mixture gave $[M(CN)_3O(L–L)]^-$ (L–L = Schiff base ligand), isolated as $[AsPh_4]^+$ salts. The complexes have been characterized by elemental analysis, and electronic, i.r. and ^{1}H-n.m.r. spectroscopy. The Schiff base ligands complex in a bidentate manner through the two nitrogen atoms giving mixed-ligand compounds similarly to 2,2′-bipyridyl or 1,10-phenanthroline.

Introduction

It is now well established that the *trans*-tetracyanodioxomolybdates(IV) and -tungstates(IV), $[M(CN)_4O_2]^{4-}$, undergo the following stepwise protonation reactions:

$$\underset{(1)}{[M(CN)_4O_2]^{4-}} + H^+ \overset{K_1}{\rightleftharpoons} \underset{(2)}{[M(CN)_4O(OH)]^{3-}} \quad (1)$$

$$\underset{(2)}{[M(CN)_4O(OH)]^{3-}} + H^+ \overset{K_2}{\rightleftharpoons} \underset{(3)}{[M(CN)_4O(OH_2)]^{2-}} \quad (2)$$

where M = Mo or W. The pK_1 value is > 13 or equal to 11.6, and the pK_2 values are 9.70 and 7.76 for the molybdenum(IV) and tungsten(IV) complexes (ionic strength $I = 0.5$, $t = 20\,^{\circ}C$), respectively(1,2). It is also known that the aqua complexes *(3)* react with a variety of monodentate ligands resulting in displacement of the coordinated water molecules(3,4):

$$\underset{(3)}{[M(CN)_4O(OH_2)]^{2-}} + L^{n-} \rightleftharpoons \underset{(4)}{[M(CN)_4O(L)]^{(2+n)-}} + H_2O \quad (3)$$

where $n = 0$ or 1, L = F^-, N_3^-, CN^-, NCS^- or py (pyridine). The reaction of *(3)* with bidentate ligands results in the displacement of the aqua as well as a cyano ligand(5–7):

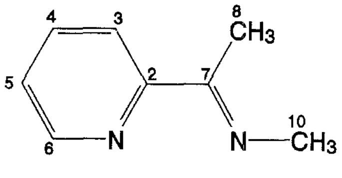
$$\underset{(3)}{[M(CN)_4O(OH_2)]^{2-}} + L\text{–}L^{n-} \rightleftharpoons \underset{(5)}{[M(CN)_3O(L\text{–}L)]^{(1+n)-}} + CN^- + H_2O, \quad (4)$$

where L–L = bipy (2,2′-bipyridyl), phen (1,10-phenanthroline) or pic (pyridine-2-carboxylate ion). The formation of *(5)* was confirmed by means of a crystal structure determination(5,6). These complexes show some very interesting properties. Their electronic spectra are dominated by intense metal-to-ligand charge transfer (MLCT) bands, whose maxima are strongly affected by the nature of the solvent(6,8) and, to a lesser extent, by the pressure(9).

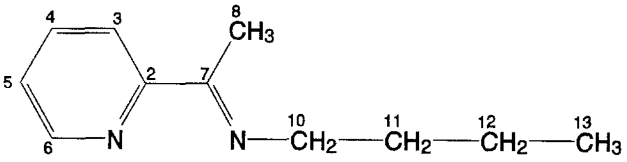
More recently, the range of mixed-ligand cyano complexes of transition metals [e.g. iron(II)] has been extended to cover pyridyl Schiff base ligands instead of bipy or phen(10). The current authors considered that it was of interest to examine the reactivity of *(3)* towards such bidentate Schiff-base ligands, which may act as analogues of polypyridines.

In this paper the synthesis and properties of new molybdenum(IV) and tungsten(IV) complexes of type *(5)* are described, where L–L are the ligands formed by condensation of 2-acetylpyridine with methyl- or butylamine, designated mesb and busb, respectively (Figure 1).

This *in situ* ligand synthesis and complex formation seems to be a very good and simple synthetic route for the preparation of such chelation-stabilized complexes of tetravalent molybdenum and tungsten.



mesb



busb

Figure 1. The formulae of the Schiff-base ligands together with the numbering of the carbon atoms.

Experimental

Materials

The initial Mo^{IV} and W^{IV} complexes, $NaK_3[M(CN)_4O_2]\cdot 6H_2O$, were prepared as described elsewhere(3). *N*-[1-(2-pyridinyl)ethylidene]-butanamine (busb) was obtained by the literature procedure(11) and was used as a crude product for preparative purposes. 2-Acetylpyridine (Fluka,

---

* On leave from the Faculty of Chemistry, Jagiellonian University, Kraków.

† Authors to whom all correspondence should be directed.

0340–4285

Table 1. Syntheses, analytical data and selected i.r. frequencies of the $[M(CN)_3O(L–L)]^-$ complexes and the non-coordinated Schiff base (busb)

Complex	Yield (%)	Found (Calcd.)(%) C	N	H	H_2O[b]	I.r. bands[a] $\nu(C{\equiv}N)$	$\nu(M{=}O)$	$\nu(C{=}N)$	Schiff-base bands
$AsPh_4[Mo(CN)_3O(mesb)]\cdot H_2O$ *(6)*	52	58.7 (57.9)	9.7 (9.7)	4.3 (4.4)	2.5 (2.5)	2098s 2110w	961vs	1600m	1254vw, 1329w, 1440s, 1470 1544vw, 1582vw, 2921vw
$AsPh_4[W(CN)_3O(mesb)]\cdot H_2O$ *(7)*	39	51.8 (51.7)	8.2 (8.6)	3.6 (4.0)	– –	2095s 2111w	955vs	1600m	1252vw, 1343m, 1440s, 1467 1515vw, 1581vw, 2921vw
$AsPh_4[Mo(CN)_3O(busb)]\cdot H_2O$ *(8)*	36	60.5 (59.5)	9.1 (9.1)	4.8 (5.0)	2.3 (2.3)	2099s 2111vw	960vs	1600m	1254vw, 1325m, 1440s, 1472 1544vw, 1581vw, 2871vw, 29
busb									1240w, 1357m, 1435s, 1467v 1567m, 1586s, 2871m, 2929v

[a] v, Very; s, strong; m, medium; w, weak; [b] amount of water determined by thermogravimetric analysis.

Switzerland) and other reagents and solvents (POCH, Poland) were used as supplied.

Generic synthesis of $[M(CN)_3O(L–L)]^-$ complexes

The following is the preferred method of synthesis of $AsPh_4[M(CN)_3O(L–L)]\cdot H_2O$ (M = Mo or W; L–L = mesb or busb). To a solution of 1.5 mmol (0.15 cm^3) of 2-acetylpyridine and 3 mmol of $MeNH_2$ (0.5 cm^3 of 25% aqueous solution) or 1.5 mmol (0.1 cm^3) of $BuNH_2$ in MeOH, 1 mmol [0.480 g (Mo) or 0.570 g (W)] of solid $NaK_3[M(CN)_4O_2]\cdot 6H_2O$ was added, and then sufficient water to dissolve the complex (*ca* 20 cm^3). The pH of the solution was adjusted to 7 with 1 M HCl. It was allowed to stand for 1 h at ambient temperature (Mo) or at 40 °C (W). $AsPh_4Cl$ was then added as a solid (2 mmol, 0.840 g) to the solution with constant stirring (to dissolve the reagent) and it was allowed to stand to 5 °C overnight (mesb) or for 2 days (busb). The resulting precipitate was filtered off, washed with cold water and dried in air *via* suction. (In the case of the W-busb system under these conditions the precipitate was not formed.) The analytical data and yields for the isolated complexes are shown in Table 1.

Physical measurements

I.r. (Brüker IFS 48), u.v.–vis. absorption (Shimadzu 2101 PC) and e.s.r. (Se/X-25, Poland) spectra were recorded in the normal manner. Thermogravimetric analyses (t.g.a.) and differential thermal analyses (d.t.a.) were performed under Ar with a heating rate of 2 °C min^{-1} on a Mettler thermoanalyser. ^{1}H-n.m.r. measurements (in CD_3CN) were performed using a Tesla BS-567 A spectrometer.

Results and discussion

Synthesis and characterization of the complexes

Reaction of $[M(CN)_4O(OH_2)]^{2-}$ with 2-acetylpyridine (acpy) and alkylamine in a water–methanol solution followed by addition of $AsPh_4Cl$ gave dark violet, diamagnetic (e.s.r.) crystals of $AsPh_4[M(CN)_3O(L–L)]\cdot H_2O$. The following salts have been isolated: $AsPh_4[Mo(CN)_3O(mesb)]\cdot H_2O$ *(6)*, $AsPh_4[W(CN)_3O(mesb)]\cdot H_2O$ *(7)* and $AsPh_4[Mo(CN)_3O(busb)]\cdot H_2O$ *(8)*.

The formation of the Schiff base in the presence of the metal (Reaction 5) seems to occur *via* coordination of bidentate 2-acetylpyridine and nucleophilic attack of the amine nitrogen on C(7):

$$[M(CN)_4O(OH_2)]^{2-} + acpy + RNH_2 \longrightarrow [M(CN)_3O(L\text{–}L)]^- + CN^- + 2H_2O \qquad (5)$$

This finds support in the significant changes of the vis. spectrum for $[Mo(CN)_4O(OH_2)]^{2-}$ solution after addition of 2-acetylpyridine alone. A similar mechanism was proposed for the reaction of salicylaldehyde with amines(12).

The thermograms of salts *(6)* and *(8)* show that dehydration takes place in one distinct step at *ca* t_{max} = 70 °C. The weight loss measurements indicate that one water molecule mol^{-1} of the complex is liberated. The anhydrous complexes are stable up to *ca* 190 °C *(6)* and 120 °C *(8)*, above which temperatures decomposition occurs.

The complexes are readily soluble in polar organic solvents, sparingly soluble in water and insoluble in non-polar solvents. Neutral aqueous solutions are relatively stable, but in acidic and basic solutions the complexes decompose. In solution they are light sensitive.

Electronic absorption spectra

Transition metal complexes with polypyridyl ligands have remarkable properties connected with long-lived d–π* metal-to-ligand charge transfer (MLCT) excited states(5,6). The Schiff bases mesb and busb (Figure 1), containing one pyridyl ring and an imine side chain, are similar to bipy. The vis. spectra of *(6)*, *(7)* and *(8)* (Figure 2, Table 2) consist of three main bands assigned to MLCT transitions, and closely resemble those of $[M(CN)_3O(bipy)]^-$ (6). All of the bands, but especially the most intense band II, are solvent dependent, in agreement

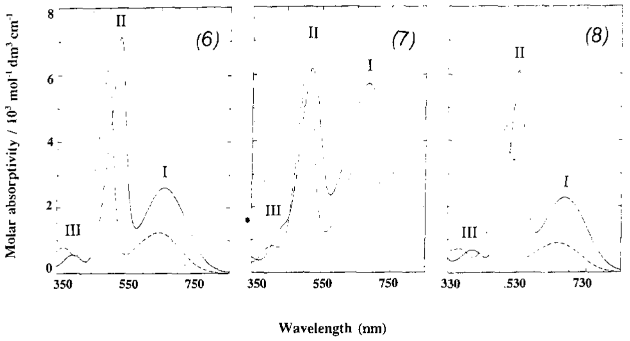


Figure 2. Electronic absorption spectra of complexes *(6)*, *(7)* and *(8)* in acetone (solid line) and methanol (dashed line).

Table 2. Absorption maxima [λ_{max} (nm)] and molar absorption coefficients [ε_{max} (10^3 dm^3 mol^{-1} cm^{-1})] for the complexes in various solvents

Solvent	*(6)*		*(7)*		*(8)*	
[(E_T (kJ mol^{-1})]	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
Water			366	–		
(264)	462	–	488	–	464	–
	652	–	662	–	649	–
Ethylene	360	–	403	–	346	–
(236)	490	–	506	–	494	–
	650	–	675	–	651	–
Methanol	362	0.85	411	0.83	361	0.72
(232)	494	6.10	508	6.89	497	4.44
	644	1.26	674	3.81	647	0.89
Ethanol	369	0.71	415	–	363	–
(217)	499	6.15	511	–	503	–
	646	1.34	679	–	645	–
n-Butanol	376	–	420	–	375	–
(210)	506	–	516	–	510	–
	647	–	681	–	650	–
Isopropanol	376	–	420	–	377	–
(203)	509	–	516	–	513	–
	650	–	682	–	651	–
t-Butanol	377	–	426	–	392	–
(184)	518	–	518	–	521	–
	651	–	685	–	660	–
Acetonitrile	378	0.69	429	1.10	380	0.67
(193)	515	7.32	519	7.52	518	6.05
	656	1.82	683	5.38	659	1.49
DMSO	380	–	434	–		–
(188)	520	–	520	–	525	–
	661	–	689	–	663	–
DMF	390	–	440	–	392	–
(183)	528	–	522	–	530	–
	660	–	685	–	663	–
Acetone	396	0.57	442	1.45	401	0.68
(177)	531	7.13	522	6.22	535	6.13
	664	2.62	684	5.74	668	2.29

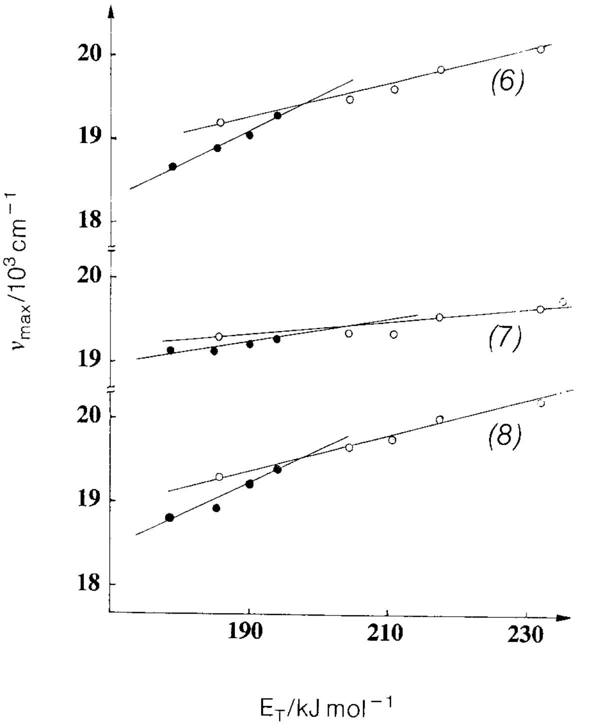


Figure 3. Second maximum wavenumber as a function of E_T value of solvent for the complexes; ○, hydroxylic solvents; ●, non-hydroxylic solvents.

with their MLCT character. The band maxima show linear dependence on the Reichardt E_T solvent parameter(13), taken as an empirical measure of solvent polarity (Figure 3). As often happens for inorganic complexes, there are two different correlation lines, for hydroxylic and non-hydroxylic solvents. This emphasizes the difference in hydrogen-bonding properties between the organic betaine used as the reference for the E_T scale, and the complexes(14). Comparison of the solvent sensitivities of *(6)*, *(7)* and *(8)* with $[Mo(CN)_3O(bipy)]^-$ (6) (Figure 4) shows that both hydroxylic and non-hydroxylic solvents lie on one correlation line. The slopes of 0.77 *(6)*, 0.37 *(7)* and 0.76 *(8)* indicate smaller solvent sensitivities than that of $[Mo(CN)_3O(bipy)]^-$.

The longest wavelength band, probably arising from the superposition of MLCT and ligand field transitions, is less solvent dependent than the others. The absorption bands of the tungsten complex *(7)* are more intense than those of the molybdenum complexes *(6)* and *(8)*, but less solvatochromic. Similar behaviour has been observed for the $[M(CN)_3O(bipy)]^-$ complexes(6).

^{1}H-n.m.r. spectra

^{1}H-n.m.r. data are presented in Table 3; for comparison the data for busb, 2-acetylpyridine and butylamine are also included. The spectra consist of four signals in the aromatic region ($\delta = 6.7$–8.7), two of which [H(3) and H(4)] are wholly obscured by strong cation signals. In the aliphatic range ($\delta = 0.9$–4.4) there are two singlets from the —CH_3 groups (mesb), or a singlet, two triplets and a multiplet (busb).

For the complexes the ring proton resonances shift upfield by 0–0.6 compared to free busb, suggesting an increase of electron density upon coordination. It is interesting that this effect is stronger for the tungsten complex.

The chemical shifts of the aliphatic protons are even more affected by coordination. The signals for H(8) shift

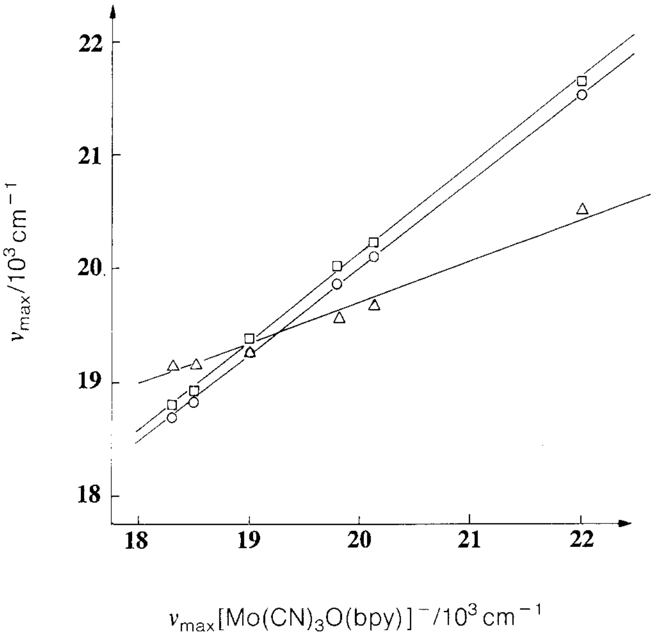


Figure 4. Correlation of frequencies of maximum absorption for the principle MLCT band (band II of Figure 2) of *(6)* (□), *(7)* (△) and *(8)* (○) with the respective values for $[Mo(CN)_3O(bipy)]^-$.

Table 3. ^{1}H-n.m.r. spectral data [δ (p.p.m.)] for the complexes in comparison to busb and its components[a]

Compound	Protons[b]							
	3	4	5	6	8	10	11,12	13
n-Butylamine	–	–	–	–	–	2.58t	1.38s	0.90t
2-Acetylpyridine	7.95d	7.82t	7.54t	8.68d	2.65s	–	–	–
busb	8.07d	7.75t	7.33t	8.55d	2.30s	3.50t	1.9–1.2m	0.96t
(6)	c	c	7.20t	8.50d	2.78s	4.12s	–	–
(7)	c	c	6.72t	8.51d	3.82s	4.22s	–	–
(8)	c	c	7.15t	8.52d	2.75s	4.39t	1.8–1.2m	0.99t

[a]s, Singlet; d, doublet; t, triplet; m, multiplet; [b]protons attached to carbon atoms with numbers shown in Figure 1; [c]resonances obscured by those of $[AsPh_4]^+$.

downfield by *ca* 0.5 p.p.m. for the molybdenum complexes and 1.5 p.p.m. for the tungsten complex. The H(10) resonances are shifted by *ca* 0.7 p.p.m. downfield in comparison to non-coordinated busb. These results indicate a significant decrease in electron density on the side-chain nitrogen. Again, this effect seems to be stronger for the tungsten complex.

I.r. spectra

The i.r. spectral data for the complexes (Table 1) are typical for the coordinated Schiff base, cyanide and oxygen. A band at 1600 cm^{-1} is associated with the imine C=N stretching. This band is shifted to lower wave numbers (by 40 cm^{-1}) in comparison to free busb, indicating that the C=N bond is weakened when the nitrogen atom is coordinated to a metal centre. The absence of a C=O stretching mode at 1700 cm^{-1} eliminates coordination of 2-acetylpyridine.

The pyridine ring stretching band is also sensitive to coordination, shifting from 1567 to 1515 (W) and 1544 (Mo) cm^{-1}. The aliphatic C—C stretching bands shift more for the molybdenum (from 1240, 1357 to 1254, 1329 cm^{-1}) than for the tungsten complexes (shifted to 1252, 1343 cm^{-1}).

The bands at 960 and 2098 cm^{-1} are assigned to M=O and C≡N stretching, respectively. The positions of these bands are very similar to those of the bipy complexes(6), suggesting similar structures for the compounds. The bands characteristic of the tetraphenylarsonium cation are in the same positions as for $AsPh_4Cl$.

Conclusions

It has been established that tetracyanodioxo-molybdates(IV) and -tungstates(IV) react readily with 2-acetylpyridine and alkylamines resulting in the formation of new complexes of Schiff-base ligands. It has been found that these precursors are very useful in preparing such complexes of molybdenum(IV) and tungsten(IV) with various Schiff-base ligands(15). This new route seems to be especially important, taking into consideration that very few reports are available on Schiff-base complexes of tetravalent molybdenum and tungsten(16). The new complexes $[M(CN)_3O(L–L)]^-$ have similar spectroscopic properties, and seem to have similar structures to those for which L–L = bipy or phen (meridional geometrical isomer). The Schiff bases mesb and busb could not be isolated from water–methanol solution in the absence of the complex, but Reaction 5 could potentially be used for the synthesis of these Schiff bases.

Acknowledgement

This work was supported in part by the Polish Research Grant Committee.

References

(1) E. Hejmo, A. Kanas and A. Samotus, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **21**, 311 (1973).
(2) A. Kanas, M. Dudek and A. Samotus, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **24**, 43 (1976).
(3) M. Dudek and A. Samotus, *Transition Met. Chem.*, **10**, 271 (1985).
(4) S. S. Basson, J. G. Leipoldt, I. M. Potgieter and A. Roodt, *Inorg. Chim. Acta*, **103**, 121 (1985); J. G. Leipoldt, S. S. Basson, A. Roodt and I. M. Potgieter, *S. Afr. J. Chem.*, **39**, 179 (1986); J. G. Leipoldt, R. van Eldik, S. S. Basson and A. Roodt, *Inorg. Chem.*, **25**, 4639 (1986); A. Roodt, J. G. Leipoldt, S. S. Basson and I. M. Potgieter, *Transition Met. Chem.*, **13**, 336 (1988); I. M. Potgieter, S. S. Basson, A. Roodt and J. G. Leipoldt, *Transition Met. Chem.*, **13**, 209 (1988); A. Roodt, J. G. Leipoldt, S. S. Basson and I. M. Potgieter, *Transition Met. Chem.*, **15**, 439 (1990); J. G. Leipoldt, S. S. Basson, A. Roodt and W. Purcell, *Polyhedron*, **11**, 2277 (1992).
(5) J. G. Leipoldt, S. S. Basson, A. Roodt and I. M. Potgieter, *Transition Met. Chem.*, **11**, 323 (1986); S. S. Basson, J. G. Leipoldt and I. M. Potgieter, *Inorg. Chim. Acta*, **87**, 71 (1984); S. S. Basson, J. G. Leipoldt and I. M. Potgieter, *Inorg. Chim. Acta*, **90**, 57 (1984).
(6) J. Szklarzewicz, A. Samotus, N. W. Alcock and M. Moll, *Transition Met. Chem.*, **15**, 2959 (1990).
(7) A. Samotus, A. Kanas, W. Glug, J. Szklarzewicz and J. Burgess, *Transition Met. Chem.*, **16**, 614 (1991).
(8) A. Al-Alousy, J. Burgess, A. Samotus and J. Szklarzewicz, *Spectrochim. Acta*, **47A**, 985 (1991).
(9) B. Burda, A. Samotus, J. Szklarzewicz, J. Burgess and S. A. Parsons, Unpublished work.
(10) R. Bin Ali, J. Burgess, M. Kotowski and R. van Eldik, *Transition Met. Chem.*, **12**, 230 (1987); J. Burgess, S. Radulović and F. Sanchez, *Transition Met. Chem.*, **12**, 529 (1987); M. Kotowski, R. van Eldik, R. Bin Ali, J. Burgess and S. Radulović, *Inorg. Chim. Acta*, **131**, 225 (1987).
(11) L. Banting and T. A. Crabb, *Magn. Res. Chem.*, **25**, 696 (1987).
(12) R. H. Holm, G. W. Everett and A. Chakravorty, *Progress in Inorganic Chemistry*, **7**, 83 (1966).
(13) J. R. Haak and J. B. F. N. Engberts, *Recl. Trav. Chim. Pays-Bas*, **105**, 307 (1986).
(14) J. Burgess, J. G. Chambers and R. I. Haines, *Transition Met. Chem.*, **6**, 145 (1981).
(15) J. Szklarzewicz, A. Samotus, J. Burgess, J. Fawcett and D. R. Russell, Unpublished work.
(16) A. Syamal and M. R. Maurya, *Coord. Chem. Rev.*, **95**, 183 (1989).

(Received 22 July 1994) TMC 3324