Structural and Spectroscopic Characterization of a Dicyanooxomolybdenum(IV) Complex with a Tetradentate Schiff-base Ligand†

Janusz Szklarzewicz,[a] **Alina Samotus,***[a] **John Burgess,***[b] **John Fawcett**[b] **and David R. Russell**[b]
[a] *Faculty of Chemistry, Jagiellonian University, R. Ingardena 3, 30–060 Kraków, Poland*
[b] *Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK*

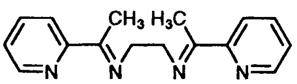
The reaction of protonated tetracyanodioxomolybdate(IV) ion with 2-acetylpyridine and ethane-1,2-diamine gave a new complex of formula $[MoO(CN)_2(L\text{–}L\text{–}L\text{–}L)]\cdot H_2O$, where L–L–L–L = *N,N'*-bis[1-(pyridin-2-yl)ethylidene]ethane-1,2-diamine. The structure of this salt was determined by X-ray analysis. Principal dimensions (ranges or means; estimated standard deviation ±0.006 Å) are Mo=O 1.689, Mo–C 2.157 and 2.168, Mo–N 2.273–2.329 Å. The crystals are monoclinic, space group *C*2/*c*, a = 31.789(2), b = 8.194(1), c = 15.198(1) Å, β = 104.08(1)°, Z = 8, R = 0.032 for 4249 observed $[F/\sigma(F) > 4]$ reflections. The molybdenum is seven-co-ordinated with the L–L–L–L ligand and oxygen in one plane and cyanide ligands above and below this plane. The structure contains water molecules which form a network of hydrogen bonds with cyanide ligands. The IR and ESR spectra, as well as the results of ion-exchange and electrophoresis experiments, are in agreement with this structure. The visible spectra in various solvents are dominated by metal-to-ligand charge-transfer bands with absorption maxima linearly dependent on the Reichardt E_T parameter. The complex undergoes one step, two-electron, reversible oxidation with $E_{\frac{1}{2}}$ = 0.77 V.

In recent years a series of mixed-ligand complexes derived from $[MO(OH_2)(CN)_4]^{2-}$ (M = Mo or W) has been synthesized and some of them characterized by means of crystal-structure determination.[1–4] Reaction with monodentate compounds gives $[MO(CN)_4L]^{n-}$ (n = 2 or 3) where L = CN^-, N_3^-, F^-, NCS^- or pyridine,[5,6] whereas that with bidentate compounds gives $[MO(CN)_3(L\text{–}L)]^{n-}$ (n = 1 or 2) where L–L = pyridine-2-carboxylate (pyca),[7] 1,10-phenanthroline (phen)[8] or 2,2'-bipyridyl (bipy).[2,9] Recently we have obtained the same type of complexes using as L–L the pyridylamine Schiff base $NC_5H_4(CR{=}NR')$-2 where R = Me and R' = Me or Bu.[10] Such complexes containing a diimine ligand exhibit intense colour due to low-lying metal-to-ligand charge-transfer (m.l.c.t.) bands which are solvato-[11] and piezo-chromic.[12]

The relatively fast reaction of $[MO(OH_2)(CN)_4]^{2-}$ with mono- and bi-dentate compounds, as well as the possibility of template generation on the metal centre of Schiff-base type ligands, prompted us to use a similar procedure to obtain complexes with tetradentate compounds. We succeeded in isolating a neutral complex $[MoO(CN)_2(L\text{–}L\text{–}L\text{–}L)]\cdot H_2O$, where L–L–L–L = *N,N'*-bis[1-(pyridin-2-yl)ethylidene]-ethane-1,2-diamine, **I**. The synthesis, crystal-structure determination, spectroscopic and electrochemical characterization of this new complex are the subject of this report. It seems also that the formation of seven-co-ordinate molybdenum(IV) species from $[MoO(OH_2)(CN)_4]^{2-}$ can help to explain why the formation of $[Mo(CN)_8]^{4-}$ from $[MoO(CN)_5]^{3-}$ is relatively slow.[1,13]

Experimental

Starting Materials.—The salt $K_3Na[MoO_2(CN)_4]\cdot 6H_2O$ was obtained as described earlier.[14] All other reagents were commercially available (analytical grade) and used as supplied.



I

Preparation of {N,N'-*Bis*[1-(*pyridin*-2-*yl*)*ethylidene*]*ethane*-1,2-*diamine*}*dicyanooxomolybdenum*(IV) *Monohydrate*, $[MoO(CN)_2(L\text{–}L\text{–}L\text{–}L)]\cdot H_2O$ **1**.—Solid $K_3Na[MoO_2(CN)_4]\cdot 6H_2O$ (3.8 g, 7.9 mmol) was dissolved (under argon) in water–Me_2CO (1 : 1, 60 cm^3) and 2-acetylpyridine (3.5 cm^3) and ethane-1,2-diamine (2.0 cm^3) were then added. The mixture was heated with stirring to 70 °C and adjusted to pH 7.0 by addition of 3 mol dm^{-3} HCl. The resulting dark pink solution was allowed to stand for 1 h at ambient temperature with argon bubbling, then the crystals were filtered off, washed with large amounts of water and then with Me_2CO. The crystals were recrystallized three times from water–Me_2CO (1 : 3). Yield *ca.* 20% (Found: C, 47.9; H, 4.8; Mo, 21.0; N, 18.5. Calc. for $C_{18}H_{20}MoN_6O_2$: C, 48.2; H, 4.5; Mo, 21.4; N, 18.8%). IR: ν(C≡N) 2110vs; ν(Mo=O) 909vs; selected bands of Schiff-base ligand, 607m, 629m, 660w, 755w, 785vs, 798m, 909vs, 1000w, 1149w, 1165w, 1257m, 1296m, 1334s, 1379w, 1431s and 1470s cm^{-1}.

Analytical Methods and Physical Measurements.—Carbon, N, H and Mo (as MoO_3 after thermal decomposition) were determined in the standard way. Infrared spectra in KBr pellets or Nujol mulls (Bruker IFS 48), UV/VIS absorption (Shimadzu 2101 PC) and ESR spectra in the solid state (SE/X25, Poland) were recorded in the normal manner. Cyclic voltammetry was performed in MeCN and water–Me_2CO mixtures with 0.1 mol dm^{-3} $NaClO_4$ as supporting electrolyte, using Pt for the working and counter electrodes and Ag–AgCl as reference electrode (PP 07, Poland). Ferrocene was used as an internal potential standard and $E_{\frac{1}{2}}$ values were calculated from the average anodic and cathodic peak potentials [$E_{\frac{1}{2}}$ = (E_a +

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

$E_c)/2]$. A cation-exchange resin (Amberlite IR 120) in the H^+ form was used in conventional ion-exchange experiments. Electrophoresis (OE 210, Hungary) was performed using silica gel plates, with aqueous 0.1 mol dm^{-3} KNO_3 as electrolyte, at 200 V.

Crystal Structure Analysis of $[MoO(CN)_2(L\text{-}L\text{-}L\text{-}L)]\cdot H_2O$.—$C_{18}H_{20}MoN_6O_2$, $M = 448.3$, monoclinic, space group $C2/c$, $a = 31.789(2)$, $b = 8.194(1)$, $c = 15.198(1)$ Å, $\beta = 104.08(1)°$, $U = 3840(1)$ Å^3, $D_c = 1.551$ g cm^{-3}, $Z = 8$, $\lambda = 0.710\,73$ Å, $T = 293$ K, $\mu = 0.71$ mm^{-1}, dark purple block, crystal dimensions 0.35 × 0.29 × 0.27 mm.

Data were collected with a Siemens P4 four-circle diffractometer in ω scan mode. Maximum 2θ was 58.9° with scan range ±0.6° and scan speed 3–30° min^{-1}. Three standard reflections were monitored every 100, and showed no deterioration during data collection. Unit-cell dimensions and standard deviations were obtained by least-squares fit of 55 reflections ($10 < 2\theta < 25°$). Reflections were processed to give 5262 unique reflections; 4249 were considered observed $[F/\sigma(F) > 4]$ and used in refinement; they were corrected for Lorentz, polarization and absorption effects from ψ scans; maximum and minimum transmission factors were 0.877 and 0.691. Systematic absences were consistent with the space group $C2/c$, which was assumed and confirmed by successful refinement. The structure was solved by direct methods. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were included in calculated positions (C–H 0.96 Å), with group refinement of isotropic thermal parameters. Final refinement was on F by least-squares methods with 248 parameters. Largest positive and negative peaks on a final Fourier-difference synthesis were of height +0.43 and −0.52 e Å^{-3}, close to the methyl carbons. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.0051$ was used, and shown to be satisfactory by weight analysis. Final $R = 0.032$, $R' = 0.055$. Maximum shift/error in final cycle 0.03. Determination of unit-cell parameters and data collection employed XSCANS[15] (Siemens). Structure solution and refinement used SHELXTL-PC.[15] Scattering factors in the analytical form and anomalous dispersion factors were those given in SHELXTL. Final atomic coordinates are given in Table 1, bond lengths and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis and Characterization of the Complex.—The reaction of the Schiff-base components on the metal centre in water–Me_2CO solution gives the Schiff-base ligand **I** which normally is difficult to synthesize under such simple conditions.[16] The reaction probably proceeds *via* co-ordination of the ethane-1,2-diamine (en) to the molybdenum in the first step (1) followed by Schiff-base condensation and co-ordination [equation (2)]. A similar overall reaction scheme

$$[MoO(OH_2)(CN)_4]^{2-} + en \longrightarrow [MoO(CN)_3(en)]^- + CN^- + H_2O \quad (1)$$

$$[MoO(CN)_3(en)]^- + 2NC_5H_4(OCMe)\text{-}2 \longrightarrow \underset{\mathbf{1}}{[MoO(CN)_2(L\text{-}L\text{-}L\text{-}L)]} + CN^- + 2H_2O \quad (2)$$

was proposed for other transition metals (*e.g.* vanadium salts with diamines and aldehydes or ketones).[17]

Complex **1** is uncharged (as shown by ion-exchange techniques and by electrophoresis), insoluble in non-polar solvents, sparingly soluble in water, Me_2CO and MeCN and freely soluble in MeOH, Me_2SO and dimethylformamide. It contains both hydrophilic (cyanide, oxide) and hydrophobic (Schiff base) ligands, and their solvation behaviour reflects the sum of the effects of these two types of ligands. In contrast to other oxocyano complexes of Mo^{IV} {*e.g.* the $[MoO_2(CN)_4]^{4-}$ anion and its protonated forms}, **1** is air-stable in the solid state and in solution (in diffused light). It is also much more stable in weakly acidic and alkaline solutions.

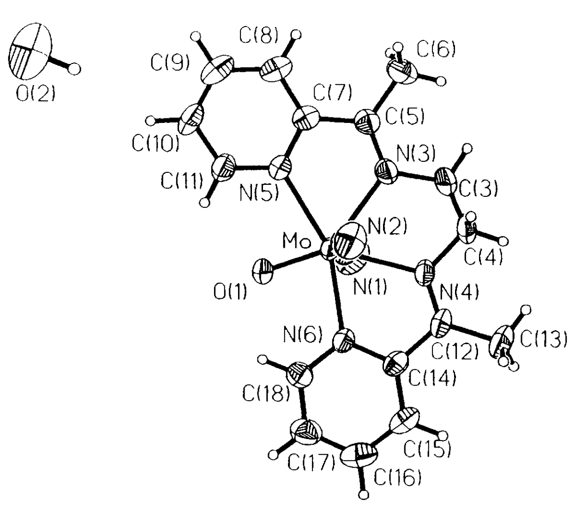


Fig. 1 Structure of $[MoO(CN)_2(L\text{-}L\text{-}L\text{-}L)]\cdot H_2O$ showing the atom numbering [C(1) and C(2) are between Mo and N(1), N(2) respectively] and 50% probability ellipsoids

The IR spectrum shows intense absorptions in the characteristic ν(C≡N) stretching region at 2110 cm^{-1}. The single stretching mode indicates not only that the cyanide ligands are equivalent but also they are essentially *trans* rather than *cis*. The ν(Mo=O) value is 909 cm^{-1} compared with 970 cm^{-1} for $[MoO(CN)_3(L\text{-}L)]^-$ (L–L = bipy[2] or phen[8]) and *ca.* 950 cm^{-1} for $[MoO(CN)_4L]^{n-}$ (L = CN^-, MeCN or N_3^-).[3,6] This noticeably lower value, despite the Mo=O bond length (Table 2) being in the same range (1.66–1.74 Å), could be related to the higher co-ordination number. We believe this to be the first example of seven-co-ordination in mixed-ligand oxomolybdenum(IV) complexes, though seven-co-ordination (distorted pentagonal bipyramid) has recently been reported in an oxotungsten(IV) complex containing a similar tetraaza ligand, 2,2′:6′,2″:6″,2‴-quaterpyridine.[18]

The ESR spectrum was consistent with our formulation of the complex.

Crystal Structure.—Complex **1** is structurally characterized as a distorted pentagonal bipyramid with equatorial oxygen and nitrogens of the Schiff-base ligand and the cyanide ligands above and below the plane (Fig. 1). The Mo–O(1) bond has a typical Mo=O distance of 1.689(2) Å, which is shorter than in $[MoO(CN)_3(bipy)]^-$ (1.735 Å),[2] but longer than in $[MoO(CN)_3(phen)]^-$ (1.659 Å).[8] The pairs of bonds are closely related to each other: Mo–N(1) and Mo–N(2) (cyano nitrogens), average 3.30 Å; Mo–N(3) and Mo–N(4) (ethane-1,2-diamine-derived nitrogens), average 2.325 Å and Mo–N(5) and Mo–N(6) (ring nitrogens) average 2.28 Å. The co-ordination polyhedron is significantly distorted (Table 2) and the angles are far from those expected for a pentagonal bipyramid [*e.g.* the C(1)–Mo–C(2) angle is 160.9°]. Both cyanide ligands participate in a network of hydrogen bonds *via* the water molecules between the complex units (Fig. 2), forming a three-dimensional net. Each water molecule links cyanide ligands in adjacent molecules of the complex; the N ··· H–O distances are 2.91 Å.

Cyclic Voltammetry.—The electrochemical properties of complex **1** were examined by cyclic voltammetry in water–Me_2CO mixtures in 0.1 mol dm^{-3} $NaClO_4$. A typical

Table 1 Atomic coordinates ($\times 10^4$) for complex **1**

Atom	*x*	*y*	*z*
Mo	3639(1)	553(1)	4794(1)
O(1)	3548(1)	1606(3)	5687(1)
C(1)	3928(1)	−1605(4)	5521(2)
N(1)	4094(1)	−2667(4)	5955(2)
C(2)	3433(1)	2320(3)	3724(2)
N(2)	3349(1)	3311(4)	3180(2)
C(3)	3658(1)	−2152(4)	3239(2)
C(4)	3958(1)	−860(5)	3037(2)
N(3)	3353(1)	−1374(3)	3692(2)
N(4)	4112(1)	106(3)	3865(2)
C(5)	2954(1)	−1801(3)	3496(2)
C(6)	2752(1)	−3016(4)	2771(2)
C(7)	2697(1)	−1037(3)	4054(2)
C(8)	2254(1)	−1279(4)	3938(2)
C(9)	2045(1)	−553(4)	4529(3)
C(10)	2281(1)	378(4)	5219(3)
C(11)	2722(1)	592(3)	5292(2)
N(5)	2931(1)	−98(3)	4724(2)
C(12)	4480(1)	856(3)	3990(2)
C(13)	4769(1)	816(5)	3347(2)
C(14)	4594(1)	1840(3)	4812(2)
C(15)	4989(1)	2639(3)	5106(2)
C(16)	5060(1)	3585(4)	5870(3)
C(17)	4733(1)	3741(4)	6309(2)
C(18)	4349(1)	2887(4)	6000(2)
N(6)	4277(1)	1913(3)	5265(1)
O(2)	862(1)	9477(4)	2378(2)

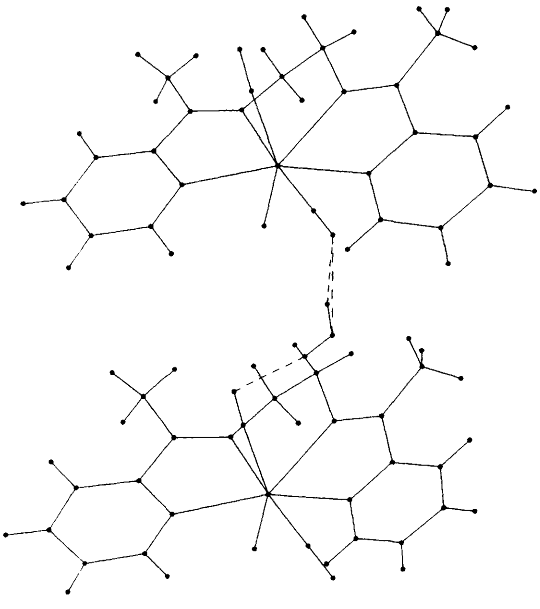


Fig. 2 Partial projection of the structure of [MoO(CN)$_2$(L–L–L–L)]·H$_2$O onto the *xy* plane; hydrogen bonds are shown as dashed lines

voltammogram[19] is presented in Fig. 3. The complex exhibits a reversible oxidative wave at 0.77 V. The peak-to-peak separation between the waves was 150 mV (independent of the scan rate between 5 and 500 mV s^{-1} and much higher than the wave separation of 86 mV observed for the ferrocenium–ferrocene couple under the same experimental conditions), and the peak current ratio (I_a/I_c) was 1.01 : 1.

The reversible redox process at $E_{\frac{1}{2}}$ = 0.77 V is presumed to be due to the essentially metal-centred Mo^{IV}–Mo^{VI} couple (two-electron process). Oxidation to the molybdenum(VI) state, but in two one-electron steps, was observed earlier in a polarographic study of the [MoO(OH)(CN)$_4$]$^{3-}$ anion.[20] The first step was found to be reversible, the second irreversible. It seems that the presence of the tetradentate ligand in **1** and the change of co-ordination number from six to seven stabilize in some degree the oxocyano-complex of Mo^{VI} making the electrochemical oxidation reversible. It should be mentioned that the only known oxocyano-complexes of M^{VI} are seven-co-ordinated [WO(CN)$_6$]$^{2-}$ and [WO(CN)$_5$(OMe)]$^{2-}$ ions.[21]

Table 2 Bond lengths (Å) and angles (°)

Mo–O(1)	1.689(2)	Mo–C(1)	2.168(3)
Mo–C(2)	2.157(3)	Mo–N(3)	2.321(2)
Mo–N(4)	2.329(3)	Mo–N(5)	2.289(2)
Mo–N(6)	2.273(2)	C(1)–N(1)	1.141(4)
C(2)–N(2)	1.143(4)	C(3)–C(4)	1.506(5)
C(3)–N(3)	1.464(4)	C(4)–N(4)	1.467(4)
N(3)–C(5)	1.280(3)	N(4)–C(12)	1.292(4)
C(5)–C(6)	1.506(4)	C(5)–C(7)	1.455(4)
C(7)–C(8)	1.389(4)	C(7)–N(5)	1.347(3)
C(8)–C(9)	1.376(5)	C(9)–C(10)	1.365(5)
C(10)–C(11)	1.390(5)	C(11)–N(5)	1.336(4)
C(12)–C(13)	1.498(5)	C(12)–C(14)	1.457(4)
C(14)–C(15)	1.389(4)	C(14)–N(6)	1.354(4)
C(15)–C(16)	1.368(5)	C(16)–C(17)	1.372(5)
C(17)–C(18)	1.386(4)	C(18)–N(6)	1.346(3)
O(2)–H(2A)	0.884	O(2)–H(2B)	0.902
O(1)–Mo–C(1)	98.1(1)	O(1)–Mo–C(2)	100.6(1)
C(1)–Mo–C(2)	160.9(1)	O(1)–Mo–N(3)	144.5(1)
C(1)–Mo–N(3)	81.7(1)	C(2)–Mo–N(3)	85.3(1)
O(1)–Mo–N(4)	145.9(1)	C(1)–Mo–N(4)	85.7(1)
C(2)–Mo–N(4)	76.7(1)	N(3)–Mo–N(4)	69.6(1)
O(1)–Mo–N(5)	78.5(1)	C(1)–Mo–N(5)	97.1(1)
C(2)–Mo–N(5)	90.4(1)	N(3)–Mo–N(5)	66.4(1)
N(4)–Mo–N(5)	135.0(1)	O(1)–Mo–N(6)	79.0(1)
C(1)–Mo–N(6)	90.2(1)	C(2)–Mo–N(6)	89.6(1)
N(3)–Mo–N(6)	136.3(1)	N(4)–Mo–N(6)	67.0(1)
N(5)–Mo–N(6)	157.1(1)	Mo–C(1)–N(1)	175.0(3)
Mo–C(2)–N(2)	175.4(2)	C(4)–C(3)–N(3)	108.3(3)
C(3)–C(4)–N(4)	107.5(3)	Mo–N(3)–C(3)	116.7(2)
Mo–N(3)–C(5)	123.0(2)	C(3)–N(3)–C(5)	120.2(2)
Mo–N(4)–C(4)	118.3(2)	Mo–N(4)–C(12)	122.1(2)
C(4)–N(4)–C(12)	118.9(3)	N(3)–C(5)–C(6)	124.8(3)
N(3)–C(5)–C(7)	114.4(2)	C(6)–C(5)–C(7)	120.8(2)
C(5)–C(7)–C(8)	124.1(2)	C(5)–C(7)–N(5)	113.6(2)
C(8)–C(7)–N(5)	122.3(3)	C(7)–C(8)–C(9)	119.4(3)
C(8)–C(9)–C(10)	118.7(3)	C(9)–C(10)–C(11)	119.2(4)
C(10)–C(11)–N(5)	123.0(3)	Mo–N(5)–C(7)	121.7(2)
Mo–N(5)–C(11)	120.5(2)	C(7)–N(5)–C(11)	117.4(2)
N(4)–C(12)–C(13)	124.9(3)	N(4)–C(12)–C(14)	114.7(3)
C(13)–C(12)–C(14)	120.4(2)	C(12)–C(14)–C(15)	123.7(3)
C(12)–C(14)–N(6)	113.5(2)	C(15)–C(14)–N(6)	122.7(2)
C(14)–C(15)–C(16)	119.4(3)	C(15)–C(16)–C(17)	118.5(3)
C(16)–C(17)–C(18)	119.8(3)	C(17)–C(18)–N(6)	122.5(3)
Mo–N(6)–C(14)	122.4(2)	Mo–N(6)–C(18)	120.6(2)
C(14)–N(6)–C(18)	116.9(2)	H(2A)–O(2)–H(2B)	109.3(1)

The chemical oxidation of complex **1** (using KMnO$_4$ in acidic solution) is irreversible.

Electronic Absorption Spectra.—The electronic absorption spectra of polypyridyl complexes of transition metals are dominated by the intense m.l.c.t. bands in the visible region.[2,11,19] The Schiff-base ligand **I** is similar to polypyridyl ligands, not only because of the nitrogen atoms as binding sites for metal ions, but also because of the presence of aromatic pyridine rings. The spectrum of complex **1** (Fig. 4) closely resembles that of the [MoO(CN)$_3$(bipy)]$^-$ anion.[2] It consists of three intense (ε > 1500 dm^3 mol^{-1} cm^{-1}) bands in the 350–750 nm range. These bands show solvent-dependent behaviour consistent with the m.l.c.t. assignment (Table 3). However, the lowest-energy band I (which has considerable d–d character) shows lower solvatochromic shifts than the next band (II) of higher energy. In Fig. 5 the wavenumbers of maximum absorbance of band II are plotted against respective values of the Reichardt E_T parameter.[22] As often for inorganic complexes, the correlation of ν_{max} with E_T shows two separate

Table 3 Absorption maxima (λ_{max}/nm) and molar absorption coefficients ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}) of [MoO(CN)$_2$(L–L–L–L)]·H$_2$O in various solvents

Solvent	E_T	λ(ε)			
Water	63.1	727	523	410	–
Methanol[a]	55.5	713 (6.13)	542 (20.3)	*b*	369 (2.34)
Diethylene glycol	53.8	717	542	*b*	367
Ethanol[c]	51.9	717 (6.36)	544 (20.0)	*b*	368 (2.20)
Butan-1-ol	50.2	722	548	*b*	374
Propan-2-ol	48.6	719	548	*b*	372
Acetonitrile	46.7	725	557	442	379
Dimethyl sulfoxide	45.0	731 (8.88)	562 (22.5)	*b*	380 (2.80)
tert-Butyl alcohol	43.9	722	552	*b*	375
Dimethylformamide	43.8	732	564	448	386
Acetone	42.2	735	564	*b*	388

[a] Other bands are: 283 (17.1) and 231 nm (26.0 dm^3 mol^{-1} cm^{-1}). [b] Shoulder. [c] Other bands are: 283 (18.4) and 231 nm (25.4 dm^3 mol^{-1} cm^{-1}).

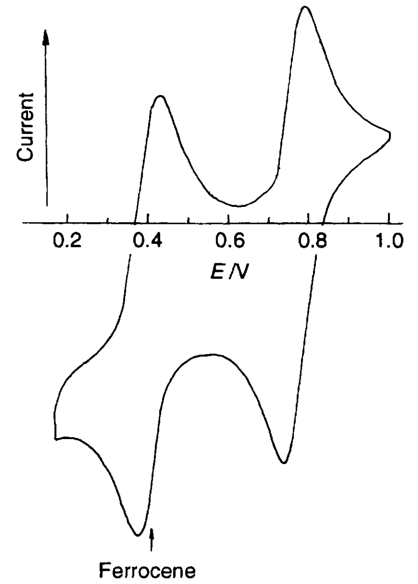


Fig. 3 Cyclic voltammogram of a 1.2 × 10^{-4} mol dm^{-3} solution (water–Me$_2$CO, 1 : 1 mixture) of [MoO(CN)$_2$(L–L–L–L)]·H$_2$O in 0.1 mol dm^{-3} NaClO$_4$ *vs.* silver chloride electrode; scan speed 50 mV s^{-1}, platinum working electrode; ferrocene as internal standard

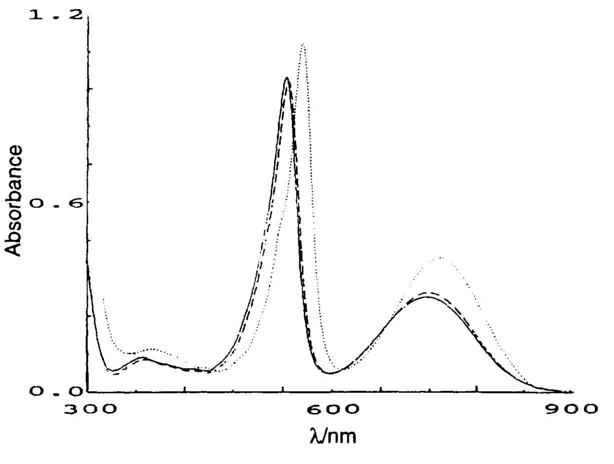


Fig. 4 Electronic absorption spectra of [MoO(CN)$_2$(L–L–L–L)]·H$_2$O in different solvents (——, MeOH; - - -, EtOH, . . ., Me$_2$SO); path-length 1 cm, [complex] = 4.92 × 10^{-5} mol dm^{-3}

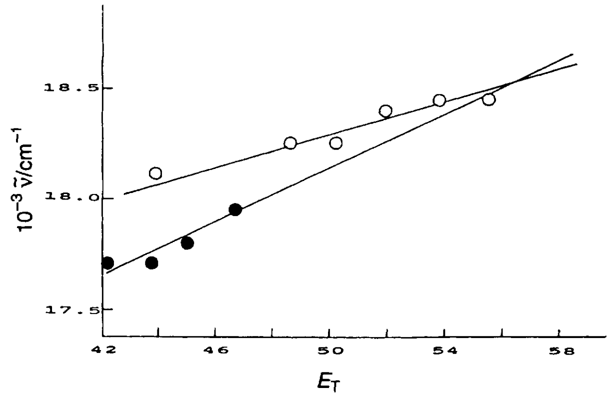


Fig. 5 Correlation of frequencies of maximum absorptions for the m.l.c.t. band II of [MoO(CN)$_2$(L–L–L–L)]·H$_2$O with solvent E_T values (○, hydroxylic solvents; ●, non-hydroxylic solvents)

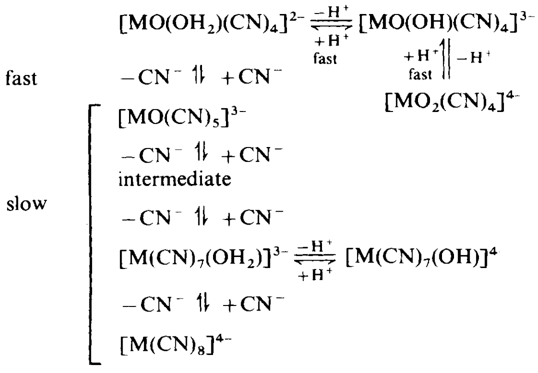
lines, for hydroxylic and non-hydroxylic solvents,[11,23] arising from the difference in hydrogen-bonding properties between **1** and the organic betaine used as the reference for the E_T scale.

The difference between the slopes of these two lines provides a good measure of relative solvatochromic effect, suggesting that the solvent sensitivities connected with the Schiff-base ligand (non-hydroxylic solvents) are greater than that based on solvent interaction with oxide and cyanide ligands (hydroxylic solvents).

A number of ternary molybdenum(0) complexes are known to be solvatochromic,[24,25] so it is of interest to compare solvent sensitivities of the molybdenum-(IV) and -(0) complexes. Probably the nearest molybdenum(0) complex equivalent to our complex is the tetracarbonylmolybdenum(0) compound with the Schiff base derived from 2-acetylpyridine and methylamine [Mo(CO)$_4$(L–L)], but its water-insolubility led us to prefer to make comparisons with the analogous, but water-soluble, complex of the closely related Schiff base derived from 2-acetylpyridine and β-alanine.[26] A plot of ν_{max}(m.l.c.t.) for our present molybdenum(IV) complex [Mo^{IV}O(CN)$_2$-(L–L–L–L)] against ν_{max}(m.l.c.t.) for the water-soluble [Mo^0(CO)$_4$(L–L)][26] gave two well separated lines, for hydroxylic and for non-hydroxylic solvents. The slope of the former was 0.41, of the latter approximately 0.3 (the four points are rather widely scattered about a much shorter best straight line). Clearly [Mo^{IV}O(CN)$_2$(L–L–L–L)] is considerably less solvatochromic than are the molybdenum(0) tetracarbonyl–Schiff base complexes. As so little is known of oxidation-state effects on solvatochromic behaviour we are unable to comment informatively on this observation.

Conclusion

The most characteristic feature of the formation of [MoO(CN)$_2$(L–L–L–L)] is the change of co-ordination number from six to seven, but not eight, which is common for homoleptic cyano-complexes of Mo^{IV} and its derivatives. This may suggest that the formation of $[M(CN)_8]^{4-}$ from $[MO_2(CN)_4]^{4-}$, which is known to occur according to Scheme 1,[1,5,13] involves as intermediate a seven-co-ordinated complex of the type $[MO(CN)_6]^{4-}$ and its protonated forms. The next stage (change of co-ordination number to eight) seems to be responsible for the relatively slow reaction of $[M(CN)_8]^{4-}$ formation ($\tau_{\frac{1}{2}} \approx 10^3$ min for the molybdenum complex) but not substitution of the aqua ligand in $[M(CN)_7(OH_2)]^{3-}$ as was suggested by Leipoldt and co-workers.[1,13] This last reaction for the tungsten analogue $[W(CN)_7(OH_2)]^{3-}$, was previously found[27] to be a relatively fast process (k_{obs} = 2.9 dm^3 mol^{-1} s^{-1}).



Scheme 1

Acknowledgements

This work was supported in part by the Polish Grant Committee (KBN).

References

1 J. G. Leipoldt, S. S. Basson, A. Roodt and W. Purcell, *Polyhedron*, 1992, **11**, 2277 and refs. therein.
2 J. Szklarzewicz, A. Samotus, N. W. Alcock and M. Moll, *Transition Met. Chem.*, 1990, 2959.
3 H. Arzoumanian, M. Pierrot, F. Ridouane and J. Sanches, *Transition Met. Chem.*, 1971, **16**, 1942.
4 K. Wieghardt, G. Backes-Dahmann and W. Holtzbach, *Z. Anorg. Allg. Chem.*, 1983, **499**, 44.
5 M. Dudek and A. Samotus, *Transition Met. Chem.*, 1985, **10**, 271 and refs. therein.
6 S. S. Basson, J. G. Leipoldt, I. M. Potgieter and A. Roodt, *Inorg. Chim. Acta*, 1985, **103**, 121; J. G. Leipoldt, S. S. Basson, A. Roodt and I. M. Potgieter, *S. Afr. J. Chem.*, 1986, **39**, 179; J. G. Leipoldt, R. van Eldik, S. S. Basson and A. Roodt, *Inorg. Chem.*, 1986, **25**, 4639; A. Roodt, J. G. Leipoldt, S. S. Basson and I. M. Potgieter, *Transition Met. Chem.*, 1988, **13**, 336; I. M. Potgieter, S. S. Basson, A. Roodt and J. G. Leipoldt, *Transition Met. Chem.*, 1988, **13**, 209; A. Roodt, J. G. Leipoldt, S. S. Basson and I. M. Potgieter, *Transition Met. Chem.*, 1990, **15**, 439.
7 J. G. Leipoldt, S. S. Basson, A. Roodt and I. M. Potgieter, *Transition Met. Chem.*, 1986, **11**, 323.
8 S. S. Basson, J. G. Leipoldt and I. M. Potgieter, *Inorg. Chim. Acta*, 1984, **87**, 71; 1984, **90**, 57.
9 A. Samotus, A. Kanas, W. Glug, J. Szklarzewicz and J. Burgess, *Transition Met. Chem.*, 1991, **16**, 614.
10 B. Burda, J. Burgess, S. Parsons, A. Samotus and J. Szklarzewicz, unpublished work.
11 A. Al-Alousy, J. Burgess, A. Samotus and J. Szklarzewicz, *Spectrochim. Acta, Part A*, 1991, **47**, 985.
12 B. Burda, A. Samotus, J. Szklarzewicz, J. Burgess and S. Parsons, unpublished work.
13 J. P. Smit, W. Purcell, A. Roodt and J. G. Leipoldt, *J. Chem. Soc., Chem. Commun.*, 1993, 1388.
14 M. Dudek, A. Kanas and A. Samotus, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1135.
15 J. Fait, XSCANS User's Manual, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1991; G. M. Sheldrick, SHELXTL-PC, Release 4.2, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1991.
16 D. H. Busch and J. C. Bailar, *J. Am. Chem. Soc.*, 1956, **78**, 1137.
17 C. A. Root, J. D. Hoeschele, C. R. Cornman, J. W. Kampf and V. L. Pecoraro, *Inorg. Chem.*, 1993, **32**, 3855.
18 S.-M. Yang, K.-K. Cheung and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1993, 3515.
19 L. M. Vogler, B. Scott and K. J. Brewer, *Inorg. Chem.*, 1993, **32**, 898 and refs. therein.
20 A. Beg, Kabir-Ud-Din and R. A. Khan, *J. Inorg. Nucl. Chem.*, 1973, **35**, 2801.
21 B. Sieklucka, N. W. Alcock, T. J. Kemp and D. J. Stufkens, *J. Chem. Soc., Dalton Trans.*, 1990, 2331.
22 C. Reichardt, *Lösungsmitteleffekte in der Organischen Chemie*, Verlag Chemie, Weinheim, 1968; C. Reichardt and E. Harbusch-Görnert, *Liebigs Ann. Chem.*, 1983, 721.
23 J. Burgess, J. G. Chambers and R. I. Haines, *Transition Met. Chem.*, 1981, **6**, 145; J. Burgess, S. Radulovic and F. Sanchez, *Transition Met. Chem.*, 1987, **12**, 529; S. Alshehri, M. J. Blandamer, J. Burgess, P. Guardado and C. D. Hubbard, *Polyhedron*, 1993, **12**, 445.
24 H. Saito, J. Fujita and K. Saito, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 863; R. bin Ali and J. Burgess, *Transition Met. Chem.*, 1993, **18**, 9.
25 R. bin Ali, J. Burgess, M. Kotowski and R. van Eldik, *Transition Met. Chem.*, 1987, **12**, 230.
26 P. Banerjee and J. Burgess, *Inorg. Chim. Acta*, 1988, **146**, 227.
27 B. Sieklucka and A. Samotus, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1003.

Received 24*th March* 1995; *Paper* 5/01911G