Synthesis and Characterisation of Neutral Tris(bidentate) Vanadium(v) Complexes containing $N_3S_2^{3-}$ and Catecholate Ligands

Themistoklis A. Kabanos[a] **and J. Derek Woollins***[,b]
[a] *Department of Inorganic Chemistry, Section of Inorganic and Analytical Chemistry, University of Ioannina, 45110 Ioannina, Greece*
[b] *Department of Chemistry, Imperial College, South Kensington, London SW7 2AY, UK*

The preparation and characterisation of complexes of the type $[V(N_3S_2)Cl_2L]$ (L = 2,2′-bipyridyl, **1**; or 1,10-phenanthroline, **2**) and $[V(N_3S_2)L(L')]$ [L′ = catecholate (cat) or 3,5-di-*tert*-butylcatecholate (dtbc)] **3–6** is described. The new complexes have been characterised by microanalyses, ^{51}V NMR, IR and visible spectroscopy as well as electrochemistry. All the new complexes are air stable as solids. Complexes **3** and **4** have a one-electron reversible couple and an anodic peak, whereas the dtbc complexes **5** and **6** have two one-electron reversible redox couples. The ^{51}V NMR spectra of **1–6** are characteristic, in particular there is a large downfield shift on replacing cat by dtbc.

The chemistry of V^{IV} and V^{V} is dominated by the vanadyl and divanadyl ($VO^{2,3+}$, VO_2^{+}) species[1,2] and a variety of these compounds, with square-pyramidal[3–5] and distorted-tetrahedral geometries,[6] are most well known. In contrast, only a few non-oxo, the so-called bare vanadium species, with fully chelating ligands have been structurally characterised[7–9] and there is only a single example of a fully characterised anionic vanadium(V) complex.[10] The biological significance of these systems has been illustrated.[8] The trianionic chelate ligand $S_2N_3^{3-}$ offers the potential for stabilising high oxidation states for early transition metals and a number of simple systems in which the metal is complexed by this ligand and a halide have been reported.[11–14] The synthesis of mixed-ligand complexes containing both S–N and more conventional catecholate and N,N donor ligands offers the opportunity to stabilise bare V^{V} and V^{IV} as well as to gain insight into the electronic properties of the S–N ligand. Here, we describe the results of our studies into the preparation of compounds of the type $[V(N_3S_2)L(L')]$ [L = 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bipy); L′ = catecholate (cat) or 3,5-di-*tert*-butylcatecholate (dtbc)]. The new compounds have been characterised by IR and visible spectroscopy, electrochemistry and ^{51}V NMR spectroscopy. The X-ray structure of one example was reported in a preliminary communication.[15]

Experimental

General.—All procedures were performed under argon using standard Schlenk techniques or in a glove-box. Diethyl ether, toluene and triethylamine were purified by refluxing over sodium and distillation under N_2. Dichloromethane, chloroform, acetonitrile and nitromethane were refluxed over powdered calcium hydride and distilled under N_2. Chemicals came from Aldrich. Catechol was recrystallised twice from toluene; 3,5-di-*tert*-butylcatechol was recrystallised twice from pentane, 2,2′-bipyridyl was recrystallised from ethanol and phenanthroline was used as received. The compounds $[V(S_2N_3)Cl_2]$ and [V(cat)(bzac)$_2$] (bzac = 1-phenylbutane-1,3-dionate) were prepared by the literature procedures.[16,17] The purity of all starting materials was checked by elemental analysis and IR spectroscopy. Analyses for C, H, N and S were performed by the Imperial College Microanalytical Service.

Infrared spectra were measured as KBr discs or Nujol mulls on a PE1720X Fourier-transform infrared (FTIR) spectrometer, visible spectra in septum-sealed cuvettes using a Philips PU8740 instrument, ^{51}V NMR spectra using a Bruker WM250 spectrometer operating at 65.8 MHz with $VOCl_3$ as reference and fast atom bombardment (FAB) mass spectra using a VG 2020 instrument and a thiodiethanol matrix.

Electrochemical measurements were performed with a Metrohm E506 Polarecord-VA scanner and Houston 2000 recorder. Platinum-wire† and dropping-mercury electrodes were employed as working electrodes for the cyclic voltammetry and polarographic studies respectively. Platinum wire was used as the auxiliary electrode and a calomel electrode in $[NBu_4][BF_4]$-saturated CH_2Cl_2 or MeCN was used as the reference; 0.1 mol dm^{-3} $[NBu_4][BF_4]$ was used as the supporting electrolyte with the solutions being 10^{-3}–10^{-4} mol dm^{-3} in complex. Values of the reduction potentials ($E_{\frac{1}{2}}$) were obtained from the intercepts of log $[(i_d - i)/i]$ *versus* E plots. The number of electrons involved in the reversible electrode processes were estimated from the slopes of such plots according to the Heyrovsky–Ilkovic equation $\{E = E_{\frac{1}{2}} + (RT/nF) \ln [(i_d - i)/i]\}$. All potentials are reported relative to the normal hydrogen electrode (NHE)[18] and were referenced using ferrocene (+0.400 V *versus* NHE).[19]

Preparation of the Complexes.—$[V(N_3S_2)Cl_2(bipy)]$ **1**. A solution of bipyridine (0.72 g, 4.6 mmol) in dichloromethane (30 cm^3) was added dropwise to a stirred suspension of $[V(N_3S_2)Cl_2]$ (1.00 g, 2.2 mmol) in dichloromethane (15 cm^3). Upon addition of the base the sky-blue colour of the solution changed to green-yellow and finally to orange-red with a brick-red precipitate. Stirring was continued for 4 h. The solid was filtered off, washed with dichloromethane (2 × 20 cm^3) and dried *in vacuo*. Yield 1.45 g (86%) (Found: C, 31.20; H, 2.05; N, 18.10; S, 16.70. Calc.: C, 31.25; H, 2.10; N, 18.25; S, 16.70%). Mass spectrum: *m/z* 384 (M^+), 379 [VO(bipy)$_2$] and 313 $[V(N_3S_2)(bipy)]$.

The analogous phen complex **2** was prepared in a similar fashion. Yield 90% (Found: C, 35.20; H, 2.00; N, 17.10; S, 17.20. Calc.: C, 35.30; H, 2.00; N, 17.25; S, 15.70%). Mass spectrum: *m/z* 408 (M^+), 427 [VO(phen)$_2$] and 337 $[V(N_3S_2)(phen)]$.

$[V(N_3S_2)(cat)(bipy)]$ **3**. A solution of catechol (0.143 g,

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† The working electrode was cleaned by cycling in 0.1 mol dm^{-3} $HClO_4$ between −0.2 and +1.3 V at 100 mV s^{-1}.

Table 1 Infrared spectral data (cm^{-1}) for the phenanthroline complexes*

$[V(N_3S_2)Cl_2(phen)]$

1625w, 1579w, 1515m, 1495w, 1423s, 1400m, 1342w, 1304vw, 1253vw, 1224w, 1145m, 1140m, 1106m, 1050vw, 963s, 868w, 852s, 783w, 778vw, 734m, 726s, 669m, 645m, 627s, 539w, 512vw, 501w, 483vw, 451vw, 428m, 398s, 356m, 341s, 294m, 271m

$[V(N_3S_2)(cat)(phen)]$

1559m, 1516m, 1490vw, 1449m, 1424s, 1410m, 1343w, 1319w, 1307m, 1275m, 1250s, 1221w, 1209vw, 1140m, 1100m, 1012m, 980s, 962m, 908vw, 870m, 843s, 796m, 771vw, 737s, 723s, 667w, 648m, 637m, 605s, 526w, 504s, 456m, 429m, 415m, 379m, 334w, 318w

$[V(N_3S_2)(dtbc)(phen)]$

2947m, 2914m, 2866m, 1624w, 1579m, 1553w, 1545s, 1493w, 1479w, 1459w, 1424s, 1406m, 1384vw, 1355m, 1351m, 1319m, 1306vw, 1292s, 1258m, 1233m, 1222m, 1208m, 1145w, 1107m, 1091vw, 1050vw, 1029m, 996s, 986vw, 959w, 915w, 905vw, 869m, 855w, 843s, 828w, 811vw, 770m, 747w, 734m, 724s, 682w, 671w, 660w, 645m, 594s, 557vw, 541w, 522m, 502m, 478m, 451w, 426m, 408m, 384w, 351w, 322w

* KBr disc; s = strong, m = medium, w = weak and v = very.

Table 2 Visible and ^{51}V NMR spectral data for the dichloro and fully chelated vanadium(V) complexes*

Complex	λ_{max}/nm (ε/$dm^3\ mol^{-1}\ cm^{-1}$)	$\delta(^{51}V)$	$\nu_{\frac{1}{2}}$/Hz
$[V(N_3S_2)Cl_2(bipy)]$	358 (5100), 389(sh) (3900)	341	25
$[V(N_3S_2)Cl_2(phen)]$	356 (4550), 384(sh) (3630)	335	25
$[V(N_3S_2)(cat)(bipy)]$	361(sh) (6176), 431 (5580), 635(sh) (3648), 781 (3005)	579	45
$[V(N_3S_2)(cat)(phen)]$	348(sh) (7362), 420 (6363), 586(sh) (3999), 788 (3090)	595	50
$[V(N_3S_2)(dtbc)(bipy)]$	344(sh) (5484), 429 (4480), 540 (3810), 815 (3120)	780	35
$[V(N_3S_2)(dtbc)(phen)]$	344(sh) (5859), 422(sh) (4629), 542 (3904), 821 (3235)	783	35

* Dichloromethane was used as a solvent and the concentration of the solutions was 1 mmol dm^{-3}.

1.3 mmol) and triethylamine (0.263 g, 2.6 mmol) in dichloromethane (20 cm^3) was added with stirring to a suspension of compound **1** (0.500 g, 1.3 mmol) in dichloromethane (20 cm^3). Upon addition of the catechol–triethylamine the solution became black-green and a black precipitate was formed. Stirring was continued for 5 h. The precipitate was filtered off, washed with dichloromethane (2 × 10 cm^3) and dried *in vacuo*. Yield 0.40 g (55%) (Found: C, 45.40; H, 2.80; N, 16.50; S, 15.15. Calc.: C, 45.60; H, 2.85; N, 16.60; S, 15.20%). Mass spectrum: *m/z* 423 $[V(cat)_2(bipy)]$, 422 [*M* + H^+ or $V(cat)_2(Hbipy)$], 412 (M^+) and 311 $[VO(N_3S_2)(bipy)]$.

The phen analogue **4** was prepared in a similar fashion. Yield 70% (Found: C, 48.50; H, 2.80; N, 15.85; S, 14.30. Calc.: C, 48.55; H, 2.70; N, 15.70; S, 14.40%). Mass spectrum: *m/z* 447 $[V(cat)_2(phen)]$, 446 ($M + H^+$), 445 (M^+), 355 $[VO(cat)(phen)]$.

$[V(N_3S_2)(dtbc)(bipy)]$ **5**. A solution of 3,5-di-*tert*-butylcatechol (0.289 g, 1.3 mmol) and triethylamine (0.263 g, 2.6 mmol) in dichloromethane (10 cm^3) was added to a stirred suspension of compound **1** (0.500 g, 1.3 mmol) in dichloromethane (20 cm^3). Initially the yellow-orange colour changed to green-blue and finally to blue-black and the solution cleared. Stirring was continued for 3 h. The reaction mixture was reduced to a black gum *in vacuo* and washed with toluene (50 cm^3). The remaining black solid was triturated with nitromethane at room temperature to leave a black precipitate. This was filtered off, washed with diethyl ether (2 × 10 cm^3) and dried *in vacuo*. Yield 0.10 g (14%) (Found: C, 53.85; H, 5.25; N, 12.70; S, 11.50. Calc.: C, 54.00; H, 5.30; N, 13.15; S, 11.60%). Mass spectrum: *m/z* 649 $[V(dtbc)_2(bipy)H]$, 536 (*M* + 2H), 394 $[VO(N_3S_2)(dtbc)]$, 378 $[V(N_3S_2)(dtbc)]$, 313 $[V(N_3S_2)(bipy)]$ and 156 (bipy).

$[V(N_3S_2)(dtbc)(phen)]$ **6**. This compound was prepared in a similar fashion to **3**. Yield 30%. A second crop of the product was obtained by evaporating the filtrate and triturating with nitromethane. Combined yield 65% (Found: C, 56.00; H, 5.20; N, 12.45; S, 12.00. Calc.: C, 56.00; H, 5.05; N, 12.55; S, 11.50%). Mass spectrum: *m/z* 671 $[V(dtbc)_2(phen)H]$, 560 ($M + 2H^+$), 394 $[VO(N_3S_2)(dtbc)]$, 378 $[V(N_3S_2)(dtbc)]$, 337 $[V(N_3S_2)(phen)]$ and 180 (phen). Crystals of this compound used for X-ray analysis[15] were prepared by slow diffusion of diethyl ether into a chloroform solution.

Results and Discussion

Reaction of $[\{V(N_3S_2)(\mu\text{-}Cl)Cl\}_2]$ with phenanthroline or bipyridine proceeds smoothly with bridge opening in dichloromethane to give compounds **1** and **2** [equation (1)]. Treatment

$$[\{V(N_3S_2)Cl_2\}_2] + 2\,L \longrightarrow 2[V(N_3S_2)Cl_2L] \quad (1)$$

$$\mathbf{1}\ L = \text{bipy}$$
$$\mathbf{2}\ L = \text{phen}$$

of **1** or **2** with catecholate or di-*tert*-butylcatecholate and triethylamine effects halide displacement and formation of the mixed-ligand complexes **3**–**6** [equation (2)].

$$[V(N_3S_2)Cl_2L] + H_2L' + 2NEt_3 \longrightarrow [V(N_3S_2)L(L')] + 2[NHEt_3]Cl \quad (2)$$

	L	L′
3	bipy	cat
4	phen	cat
5	bipy	dtbc
6	phen	dtbc

The products are indefinitely stable in air in the solid state; in solution **1** and **2** immediately decompose in air although the other, fully chelated, complexes are stable in solution for several hours. Although air sensitive, dichloromethane solutions of **1** and **2** are quite stable under an inert atmosphere. Compounds **3**, **4** and **6** are not especially soluble in dichloromethane in contrast to $[NHEt_3]Cl$ thus allowing ready purification of the products in equation (2). In the case of **5** we obtained a rather low yield and there are some other, unidentified products formed. Clearly, the ease of the reaction and the stability of the new complexes shows that the $S_2N_3^{3-}$ ligand is very good at stablising high-oxidation-state 'bare' vanadium(V). The IR data for complexes **2**, **4** and **6** are given in Table 1; KBr discs and Nujol mulls gave identical results. A common feature of metal catecholates[20,21] is the intense bands at 1480–1450 and 1290–1250 cm^{-1}, which are assigned as ring stretching and ν(CO) respectively. We observe the lower-frequency vibration but the ring-stretching mode is obscured by vibrations due to bipy or phen. The ν(VN) vibration in the VN_3S_2 ring was observed at 958 cm^{-1} in the starting material as a very strong band.[16] This vibration is shifted to 962 and 963 cm^{-1} for **1** and **2** respectively and to 981 and 980 cm^{-1} for **3** and **4** respectively. In the case of the dtbc complexes, **5** and **6**, there are two overlapping bands at *ca.* 990 cm^{-1}, one band is due to ν(VN) and the other to the dtbc ligand {H_2dtbc has a strong absorption at 963 cm^{-1} which shifts to 988 cm^{-1} in $[V(dtbc)_2(bipy)]$}.[22] The electronic absorption spectra for **1**–**6** are given in Table 2. Complexes **1** and **2** are orange whilst **3**–**6** are deep green or green-black in appearance and the intense absorptions are due to ligand-to-metal charge transfer.

The complexes were also studied by d.c. cyclic voltammetry (CV) and d.c. polarography (Table 3 and Figs. 1 and 2). Cyclic voltammetry in dichloromethane reveals the presence of two

Table 3 Electrochemical data from CV and polarographic studies[a]

Complex	E_{p_c}/V	E_{p_a}/V	i_{p_c}/i_{p_a}	$\Delta E_p{}^b$/mV	$E_{\frac{1}{2}}{}^c$/V
$[V(N_3S_2)(cat)(bipy)]$	−0.59	−0.48	1.01	110	-0.54^c $(-0.58)^d$
		0.66			
$[V(N_3S_2)(dtbc)(bipy)]$	0.44	0.56	1.06	120	0.50
	−0.63	1.00		110	−0.69 (−0.74)
$[V(N_3S_2)(dtbc)(bipy)]^e$	0.46	0.50	1.00	60	0.48
	−0.60	−0.54	1.00	60	−0.57 (−0.56)
$[V(N_3S_2)(cat)(phen)]$	−0.58	−0.47	1.01	110	−0.53 (−0.59)
		0.64			
$[V(N_3S_2)(dtbc)(phen)]$	−0.78	−0.67	1.01	110	−0.70 (−0.73)
	0.38	0.49	1.01	110	0.44

[a] All potentials are *vs.* NHE. [b] $\Delta E_p = E_{p_c} - E_{p_a}$ at a scan rate of 100 mV s^{-1}. [c] $E_{\frac{1}{2}}$ calculated using the formula $0.5(E_{p_c} + E_{p_a})$ from cyclic voltammetry. [d] Values of the reduction potentials (in parentheses) were obtained from the intercepts of plots of ln $[(i_d - i)/i]$ *vs.* potential. [e] All studies performed in CH_2Cl_2 except this case in which the solvent was MeCN; none of the other complexes is soluble in MeCN.

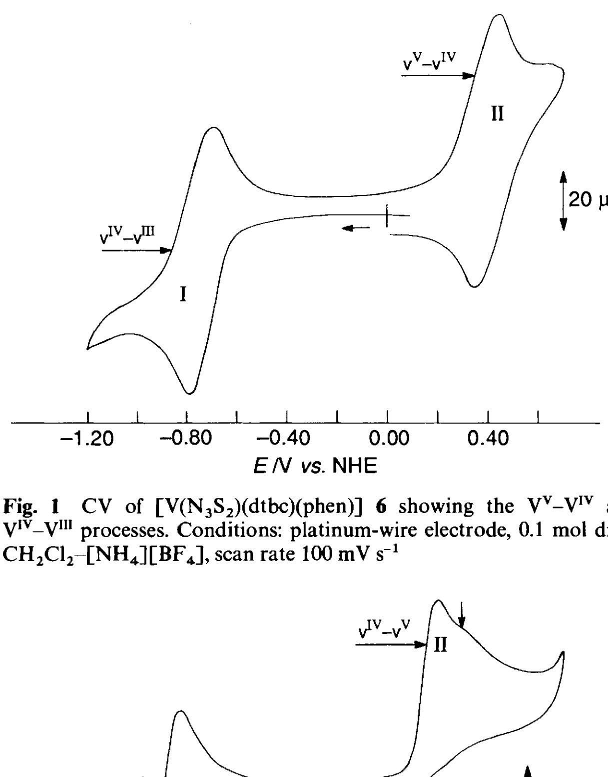

Fig. 1 CV of $[V(N_3S_2)(dtbc)(phen)]$ **6** showing the V^V–V^{IV} and V^{IV}–V^{III} processes. Conditions: platinum-wire electrode, 0.1 mol dm^{-3} CH_2Cl_2–$[NH_4][BF_4]$, scan rate 100 mV s^{-1}

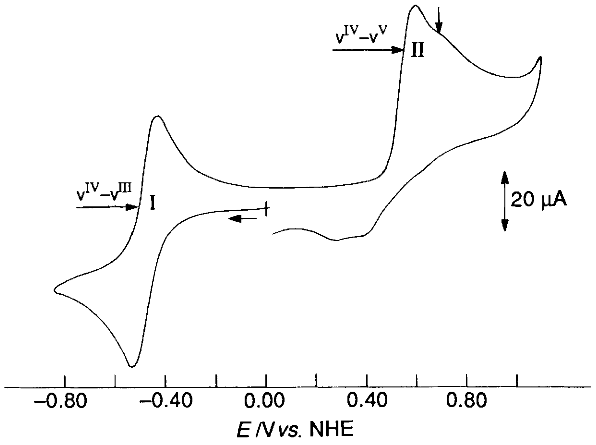

Fig. 2 CV of $[V(N_3S_2)(cat)(phen)]$ **4** showing the two redox processes at vanadium and the oxidation of the S–N ligand which is arrowed. Conditions as Fig. 1

reversible (i_{p_c}/i_{p_a} unity, ΔE_p 110 mV*) redox couples for both **5** and **6** (**5**, $E_{\frac{1}{2}}$ −0.69 and 0.50; **6**, −0.70 and 0.44 V, *vs.* NHE) (Fig. 1).* The two redox couples both have the same anodic and cathodic peak currents, which are almost independent of the scan rate up to 500 mV s^{-1}, indicating that both processes involve the same number of electrons. Polarographic studies reveal the presence of a one-electron reversible process at −0.74 and −0.73 V for **5** and **6** respectively and we thus conclude that both redox couples are one-electron reversible processes. Complex **5** was sufficiently soluble in MeCN to allow studies in this solvent where it exhibits two reversible one-electron waves (ΔE_p 60 mV). CV studies upon **3** and **4** reveal reversible redox couples at −0.54 and −0.53 V together with anodic peaks at 0.66 and 0.64 V and shoulders at 0.74 V, whilst polarography shows one-electron reversible processes at −0.58 and −0.59 V for the two complexes respectively. A blank CV run with the catecholate ligands in the potential range −1.6 to 1.3 V (*vs.* NHE) gave one peak at *ca.* +1.0 V due to oxidation of the ligand. The redox chemistry of the $S_2N_3{}^{3-}$ anion is not known since it is only stabilised in metal complexes; however it is most likely that all of the redox processes observed here are metal centred, in particular we would not expect to see a cathodic shift of *ca.* −0.2 V on going from cat to the more electron-donating dtbc if this reduction were based on the S–N ligand,† furthermore ligand-based redox processes are rarely reversible. The processes are summarised in equations (3) and (4).

$$[V^V(N_3S_2)(dtbc)(phen)] \xrightleftharpoons[-e^-]{+e^-} [V^{IV}(N_3S_2)(dtbc)(phen)]^- \quad E_{\frac{1}{2}}\ 0.44\ V \quad (3)$$

$$[V^{IV}(N_3S_2)(dtbc)(phen)]^- \xrightleftharpoons[-e^-]{+e^-} [V^{III}(N_3S_2)(dtbc)(phen)]^{2-} \quad E_{\frac{1}{2}}\ -0.70\ V \quad (4)$$

The potential data imply that the vanadium(IV) complex is the more thermodynamically stable species, although to our knowledge the $S_2N_3{}^{3-}$ ligand has only previously been observed bound to the highest oxidation state of a metal ion, except for the binuclear complex $[V(N_3S_2)Cl(py)_2]$ (py = pyridine).[13] Further studies into the isolation of the complexes of V^{IV} and V^{III} are in progress.

The ^{51}V NMR data for the complexes are given in Table 2. The starting material $[\{V(N_3S_2)(\mu\text{-Cl})Cl\}_2]$ has $\delta(^{51}V)$ −341 (half-width 206 Hz)[23] whereas all of the compounds reported here have large positive δ values. The most noticeable features are the large downfield shifts on replacing Cl by catecholate (**1** $\longrightarrow$ **3**) with further substantial downfield shifts on replacing

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* Ferrocene was used as a secondary internal reference ($E_{\frac{1}{2}}$ +0.60 V *vs.* SCE, peak separation 110 mV) by first measuring against $[V(cat)(bzac)_2]$ ($E_{\frac{1}{2}}$ −0.17 V, ΔE_p 120 mV), as a consequence of the supporting electrolyte and the method of cleaning the electrode, which was then employed as the internal reference.

† For all four fully chelated complexes there are peaks or shoulders at about 0.73 V (*vs.* NHE) and at *ca.* +1.0 V. The latter can be assigned to oxidation of the catecholato ligands. Since bipy and phen are electrochemically inert over the scan range used we assumed that the shoulder at 0.73 V is due to oxidation of the $S_2N_3{}^{3-}$ ligand.

cat by dtbc. The chemical shift range for **1**–**6** is quite large and characteristic although there is no significant difference on changing the bipy for phen. It is somewhat surprising to observe a large downfield shift on replacing cat by the more electron-*donating* dtbc.

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References

1 J. Selbin, *Coord. Chem. Rev.*, 1966, **1**, 293; D. Nicholls, *Coord. Chem. Rev.*, 1966, **1**, 379; D. A. Rice, *Coord. Chem. Rev.*, 1981, **37**, 61; 1982, **45**, 67; W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123; E. M. Page, *Coord. Chem. Rev.*, 1984, **57**, 237; R. H. Holm, *Chem. Rev.*, 1987, **87**, 1401.

2 W. A. Nugent and J. M. Mayer, *Metal-Ligand Multiple Bonds*, Wiley-Interscience, New York, 1988, pp. 159–162.

3 G. Beindorf, J. Strahle and K. Dehnicke, *Z. Naturforsch., Teil B*, 1980, **35**, 522.

4 U. Muller, A. F. Shihada and K. Dehnicke, *Z. Naturforsch., Teil B*, 1982, **37**, 699.

5 R. P. Dodge, D. H. Templeton and A. J. Zalkin, *J. Chem. Phys.*, 1961, **35**, 55.

6 D. Fenske, A. F. Shihada, H. Scwarb and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1980, **471**, 140.

7 T. W. Hambley, C. J. Hawkins and T. A. Kabanos, *Inorg. Chem.*, 1987, **26**, 3740 and refs. therein.

8 M. Carrondo, M. Duarte, J. Pessoor, J. Silvod, J. F. Silva, M. Vaz and L. Vilas-Boas, *J. Chem. Soc., Chem. Commun.*, 1988, 1158.

9 U. Auerbach, B. Della Veolova, K. Wieghardt, B. Nuber and J. Weiss, *J. Chem. Soc., Chem. Commun.*, 1990, 1004.

10 M. E. Cass, N. R. Garolon and C. G. Pierpont, *Inorg. Chem.*, 1986, **25**, 3962.

11 P. F. Kelly and J. D. Woollins, *Polyhedron*, 1986, **5**, 607; T. Chivers and F. Edelmann, *Polyhedron*, 1986, **5**, 1661; P. F. Kelly and J. D. Woollins, *Transition Met. Chem.*, 1988, **13**, 77.

12 R. Christophersen, P. Klingelhofer, U. Muller and K. Dehnicke, *Z. Naturforsch., Teil B*, 1985, **40**, 1631.

13 R. Christophersen, P. Klingelhofer, U. Muller and K. Dehnicke, *Z. Naturforsch., Teil B*, 1986, **41**, 1420.

14 A. El-Kholi, R. Christophersen, U. Muller and K. Dehnicke, *Z. Naturforsch., Teil B*, 1986, **42**, 410.

15 T. A. Kabanos, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1990, 193.

16 J. Hanich, M. Krestel, U. Muller, K. Dehnicke and D. Rehder, *Z. Naturforsch., Teil B*, 1984, **39**, 1686.

17 C. J. Hawkins and T. A. Kabanos, *Inorg. Chem.*, 1989, **28**, 1084.

18 R. R. Gagne, C. A. Koval and G. C. Lisensky, *Inorg. Chem.*, 1980, **19**, 2854.

19 H. M. Koepp, H. Wendt and H. Strehlow, *Z. Elektrochem.*, 1960, **64**, 483.

20 P. A. Wicklund and D. G. Brown, *Inorg. Chem.*, 1976, **15**, 396.

21 L. Que and R. H. Heinstand, *J. Am. Chem. Soc.*, 1979, **101**, 2219.

22 T. A. Kabanos and J. D. Woollins, unpublished work.

23 J. Anhaus, Z. A. Siddiqi, J. Schimkowiak and H. W. Roesky, *Z. Naturforsch., Teil B*, 1984, **39**, 1722.

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