Direct Electrochemical Synthesis of Pyridine-2-thionato Complexes of Nickel(II): The Crystal Structure of (2,2'-Bipyridine)bis(pyridine-2-thionato)nickel(II)–2,2'-Bipyridine(2/1)†‡

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The compound [Ni(pyt)$_2$] has been prepared in good yield by electrochemical oxidation of the metal in a solution of pyridine-2-thione (Hpyt) in acetonitrile. When pyridine (py), 2,2'-bipyridine (bipy), or 1,10-phenanthroline (phen) is present in the electrochemical cell the corresponding adducts [Ni(pyt)$_2$(py)$_2$], [Ni(pyt)$_2$(bipy)], or [Ni(pyt)$_2$(phen)] is obtained. The crystal structure of [Ni(pyt)$_2$(bipy)]·0.5 bipy is monoclinic, with a = 10.409(2), b = 12.013(3), c = 19.790(3) Å, β = 103.95(3)°, space group $P2_1/c$, and R = 0.032 for 3 176 reflections with $|I_o| > 3\sigma|I_o|$. The molecule has a distorted octahedral NiN$_4$S$_2$ kernel, with average bond distances of 2.065 Å for Ni–N and 2.485 Å for Ni–S. The vibrational and electronic spectra of the compounds are discussed.

The co-ordination of metal ions to pyridine-2-thione is of current interest, due to their use as clinically useful drugs,[1] and their important biological role, since pyridine-2-thione can be considered as a model compound for 6-thioguanosine (2-amino-1,2-dihydro-9β-D-ribofuranosyl-6*H*-purine-6-thione).[2] On the other hand, the active sites of several hydrogenases are believed to contain nickel in a distorted pseudo-octahedral or square-pyramidal environment dominated by sulphur-containing ligands, although the presence of a small number of atoms of low atomic number cannot be completely ruled out.[3–5] This has increased the interest in the synthesis of monomeric nickel thiolates.

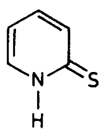
Pyridine-2-thione, which exists predominantly as the thione form (**1**) in neutral solution[6,7] and in the solid state,[8] is also of interest because of the possibility to co-ordinate to metal ions in the thione (**2**) and thionate (**3**)—(**5**) forms and to its ability to act as a unidentate (**2**),[9–11] (**3**),[11,12] bidentate (**4**),[11–13] or bridging (**5**)[10,14] ligand.

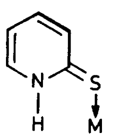
In this paper we describe the electrochemical synthesis of some thionate complexes of nickel(II) and the structure of (2,2'-bipyridine)bis(pyridine-2-thionato)nickel(II), which as far as we know is the first neutral octahedral complex of nickel(II) with bidentate thionate ligands forming four-membered S,N-chelate rings.

Experimental

Acetonitrile was dried by refluxing over phosphorus pentoxide and distilled immediately prior to use. Pyridine-2-thione (Hpyt), pyridine (py), 1,10-phenanthroline (phen), and 2,2'-bipyridine (bipy) were all commercial products and were used without further purification. Nickel (Ega Chemie) was used as plates (*ca.* 2 × 2 cm).

The electrochemical method used in the synthesis of the metal complexes was similar to that described by Tuck and co-workers.[15] The cell was a tall-form beaker (100 cm^3) fitted with a rubber bung through which the electrical leads passed. The foil anode was suspended from a platinum wire and the cathode was also a platinum wire. The ligand pyridine-2-thione was dissolved in acetonitrile and a small amount of tetramethylammonium perchlorate was added. For the synthesis of mixed complexes, the corresponding ligand (pyridine, 1,10-phenanthroline, or 2,2'-bipyridine) was added to the solution. Direct current was obtained from a purpose-built d.c. power supply. The cells can be summarized as Pt(−)|MeCN + Hpyt|Ni(+) and Pt(−)|MeCN + Hpyt + L|Ni(+), where L = py, phen, or bipy. At the end of electrolysis the products to be isolated were collected, washed with acetonitrile and diethyl ether, and dried under vacuum. The experimental conditions for the reactions are set out in Table 1.


(**1**)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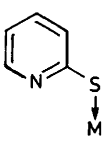
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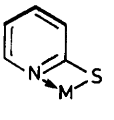
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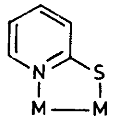
(**5**)

The C, N, and H contents of the complexes were determined on a Perkin-Elmer 240B microanalyser. Infrared spectra were recorded as KBr mulls on a Perkin-Elmer 180 spectrophotometer. The solid-state electronic spectra were recorded on a Beckman DK-2 spectrophotometer with a solid reflectance attachment using MgO as reference, solution spectra on a Uvikon 810P spectrophotometer using dimethylformamide (dmf) or MeOH as solvent.

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‡ *Supplementary data available:* further details of the structure determination have been deposited as Supplementary Publication No. CSD-53230 at the Fachinformationzentrum Energie, Physik, Mathematik, D-7514 Eggeinstein-Leopoldshafen, Federal Republic of Germany.

Table 1. Experimental conditions for the electrochemical synthesis

Amount of pyridine-2-thione (g)[a]	Amount of ligand (g)	Initial voltage (V)[b]	Time (h)	Metal dissolved (mg)	Ef (mol F^{-1})
0.18		20	2	44	0.50
0.25	0.18 (bipy)	25	3	69	0.51
0.22	0.20 (phen)	20	2.5	53	0.48
0.17	0.14 (py)	20	2	43	0.49

[a] Plus NMe_4ClO_4 (*ca.* 10 mg). [b] Voltage to produce a current of 20 mA.

Table 2. Final fractional atomic co-ordinates for $[Ni(pyt)_2(bipy)]\cdot0.5bipy$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Ni	0.141 15(3)	0.068 17(3)	0.841 39(2)
S(1)	0.311 18(8)	−0.024 66(7)	0.792 69(5)
S(2)	0.033 61(8)	−0.291 75(8)	0.654 18(4)
N(1)	0.242 4(2)	0.061 4(2)	0.945 3(1)
N(2)	0.049 9(2)	−0.065 2(2)	0.876 6(1)
N(3)	0.267 0(2)	0.181 5(2)	0.813 7(1)
N(4)	−0.001 9(2)	−0.419 7(2)	0.752 5(1)
N(5)	0.556 5(3)	0.135 0(3)	0.481 8(2)
C(1)	0.344 8(3)	0.126 9(3)	0.976 2(2)
C(2)	0.406 5(4)	0.117 4(3)	1.046 3(2)
C(3)	0.358 5(4)	0.040 4(3)	1.085 9(2)
C(4)	0.252 5(3)	−0.025 5(3)	1.054 7(2)
C(5)	0.198 5(3)	−0.014 3(3)	0.983 8(2)
C(6)	0.089 5(3)	−0.086 3(2)	0.945 1(1)
C(7)	0.033 1(3)	−0.170 7(3)	0.976 2(2)
C(8)	−0.066 0(3)	−0.235 0(3)	0.935 4(2)
C(9)	−0.105 5(3)	−0.214 9(3)	0.865 0(2)
C(10)	−0.045 3(3)	−0.129 4(3)	0.837 7(2)
C(11)	0.348 0(3)	0.115 2(3)	0.787 9(2)
C(12)	0.448 2(3)	0.160 8(4)	0.760 8(2)
C(13)	0.462 6(4)	0.274 0(4)	0.761 2(2)
C(14)	0.380 9(4)	0.341 1(3)	0.788 4(2)
C(15)	0.283 5(3)	0.292 4(3)	0.814 8(2)
C(21)	0.081 1(3)	−0.342 1(3)	0.738 2(2)
C(22)	0.193 3(3)	−0.309 4(3)	0.789 3(2)
C(23)	0.217 9(4)	−0.358 6(4)	0.853 1(2)
C(24)	0.132 4(4)	−0.438 3(4)	0.867 6(2)
C(25)	0.023 4(3)	−0.467 7(3)	0.816 1(2)
C(31)	0.637 7(4)	0.180 1(4)	0.446 5(2)
C(32)	0.705 9(4)	0.120 7(4)	0.407 9(2)
C(33)	0.692 2(4)	0.008 0(4)	0.405 9(2)
C(34)	0.611 1(4)	−0.041 9(4)	0.442 0(2)
C(35)	0.545 0(3)	0.024 2(3)	0.479 7(2)

Crystal Structure Analysis.—The electrochemically synthesized product $[Ni(pyt)_2(bipy)]$ was crystallized from acetone containing a few mg of bipy to give amber air-stable crystals of $[Ni(pyt)_2\cdot(bipy)]\cdot0.5bipy$ suitable for *X*-ray studies.

Crystal data. $C_{25}H_{20}N_5NiS_2$, $M = 513.31$, monoclinic, space group $P2_1/c$, $a = 10.409(2)$, $b = 12.013(3)$, $c = 19.790(3)$ Å, $\beta = 103.95(3)°$, $U = 2\,401.4$ Å^3, $Z = 4$, $D_c = 1.420$ g cm^{-3}, $F(000) = 1\,060$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,73$ Å, $\mu = 9.994$ cm^{-1}.

A prismatic crystal (dimensions 0.75 × 0.50 × 0.25 mm) was used for data collection on a CAD4 automated four-circle diffractometer at room temperature, by the ω—θ scan technique with graphite-monochromated Mo-K_α radiation. 4 696 Intensities recorded to $\theta_{max.}$ 25°, 4 186 unique ($R_{int} = 0.018$), of which 3 176 with $I > 3\sigma(I)$ were used in refinement. They were corrected for Lorentz polarization factors; an empirical absorption correction[16] was applied (minimum and maximum values 0.901 and 1.071). The structure was solved by direct methods. Positional and anisotropic thermal parameters for non-hydrogen atoms were refined by full-matrix least squares. Hydrogen atoms were located on a ΔF map and included in structure-factor calculations with fixed isotropic thermal parameters ($B_{iso} = 4.0$ Å^2), but were not refined. Weighting scheme $w^{-1} = \sigma^2(F)$. The agreement factor converged to $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.032$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.032$. 299 Parameters; S 1.11; maximum Δ/σ 0.025; maximum $\Delta\rho$ 0.271 e Å^{-3}; secondary extinction coefficient 2.883 1(2) × 10^{-8}.[17] Neutral scattering factors were used.[18] Computations were performed on a DEC Micro VAXII computer using SHELXS[19] and VAXSDP.[20] Final atomic co-ordinates are presented in Table 2.

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

Results and Discussion

The analytical data reported in Table 3 show that an electrochemical procedure can be satisfactorily used for the synthesis of the complex $[Ni(pyt)_2]$ and of mixed compounds of formula $[Ni(pyt)_2(py)_2]$ and $[Ni(pyt)_2L]$, where L is phen or bipy. During the electrochemical process, hydrogen was evolved at the cathode, and in the case of $[Ni(pyt)_2]$ the formation of an insoluble powder was visible within a few minutes. In the other cases crystalline compounds were obtained after several hours, and for some complexes concentration of the solution was necessary in order to obtain a solid compound.

The electrochemical efficiency, defined as the amount of metal dissolved per Faraday of charge, was close to 0.5 mol F^{-1}. The reaction mechanism can therefore be written in the Scheme.

$$\text{Cathode: } 2Hpyt + 2e^- \longrightarrow H_2(g) + 2pyt^-$$

$$\text{Anode: } 2pyt^- + Ni \longrightarrow [Ni(pyt)_2] + 2e^-$$

$$2pyt^- + Ni + nL \longrightarrow [Ni(pyt)_2L_n] + 2e^-$$

Scheme. $n = 2$, L = py; $n = 1$, L = phen or bipy

Description of the Structure.—Selected bond distances and angles are given in Table 4. The structure of $[Ni(pyt)_2(bipy)]$ is shown in the Figure 2.

The geometry of the molecule can be described as a severely distorted octahedron in which the nickel atom is co-ordinated to the bidentate 2,2′-bipyridine ligand and two bidentate pyridine-2-thionato ligands through their nitrogen and sulphur atoms, with the sulphur atoms *trans*. The nearly square equatorial plane is formed by the 2,2′-bipyridine nitrogens, with Ni–N(1) and Ni–N(2) bond distances of 2.074(2) and 2.067(3) Å, and two nitrogen atoms from the two pyridine-2-thionato ligands, with Ni–N(3) and Ni–N(4) bond distances of 2.053(3) and 2.068(2) Å. These lengths are hardly different from those

Table 3. Analytical data (%)*

Complex	Colour	C	N	H
$[Ni(pyt)_2]$	Green	42.6 (43.0)	9.6 (10.0)	2.8 (2.8)
$[Ni(pyt)_2(bipy)]$	Amber	54.7 (55.2)	12.5 (12.9)	3.7 (3.7)
$[Ni(pyt)_2(phen)]$	Brown	56.9 (57.5)	12.4 (12.2)	3.7 (3.5)
$[Ni(pyt)_2(py)_2]$	Green	54.6 (54.9)	12.3 (12.8)	4.1 (4.1)

* Required values are given in parentheses.

Table 4. Selected bond lengths (Å) and angles (°) for $[Ni(pyt)_2(bipy)]\cdot 0.5bipy$

Ni–S(1)	2.475(2)	N(3)–C(15)	1.342(4)
Ni–S(2)	2.495(1)	N(4)–C(21)	1.346(4)
Ni–N(1)	2.074(2)	N(4)–C(25)	1.351(5)
Ni–N(2)	2.067(3)	N(5)–C(31)	1.335(7)
Ni–N(3)	2.053(3)	N(5)–C(35)	1.336(5)
Ni–N(4)	2.068(2)	C(11)–C(12)	1.396(5)
S(1)–C(11)	1.730(3)	C(12)–C(13)	1.368(6)
S(2)–C(21)	1.726(3)	C(13)–C(14)	1.373(6)
N(1)–C(1)	1.348(5)	C(14)–C(15)	1.377(6)
N(1)–C(5)	1.336(5)	C(21)–C(22)	1.405(4)
N(2)–C(6)	1.343(3)	C(22)–C(23)	1.361(6)
N(2)–C(10)	1.343(4)	C(23)–C(24)	1.385(6)
N(3)–C(11)	1.347(4)	C(24)–C(25)	1.376(5)
S(1)–Ni–S(2)	155.96(3)	C(11)–N(3)–C(15)	120.3(3)
S(1)–Ni–N(1)	97.35(7)	C(21)–N(4)–C(25)	120.1(2)
S(1)–Ni–N(2)	102.23(7)	S(1)–C(11)–N(3)	112.8(2)
S(1)–Ni–N(3)	68.46(8)	S(1)–C(11)–C(12)	126.8(3)
S(1)–Ni–N(4)	95.38(8)	N(3)–C(11)–C(12)	120.5(3)
S(2)–Ni–N(1)	101.10(8)	C(11)–C(12)–C(13)	118.7(4)
S(2)–Ni–N(2)	96.48(7)	C(12)–C(13)–C(14)	120.5(4)
S(2)–Ni–N(3)	94.56(7)	C(13)–C(14)–C(15)	118.8(4)
S(2)–Ni–N(4)	67.98(8)	N(3)–C(15)–C(14)	121.3(3)
N(1)–Ni–N(2)	78.47(9)	S(2)–C(21)–N(4)	113.4(2)
N(1)–Ni–N(3)	94.95(9)	S(2)–C(21)–C(22)	126.2(3)
N(1)–Ni–N(4)	166.6(2)	N(4)–C(21)–C(22)	120.4(3)
N(2)–Ni–N(3)	168.06(9)	C(21)–C(22)–C(23)	119.0(4)
N(2)–Ni–N(4)	94.49(9)	N(4)–C(25)–C(24)	121.4(3)
N(3)–Ni–N(4)	93.9(1)	C(23)–C(24)–C(25)	118.7(3)
C(1)–N(1)–C(5)	118.7(2)	C(22)–C(23)–C(24)	120.4(3)
C(6)–N(2)–C(10)	118.3(3)		

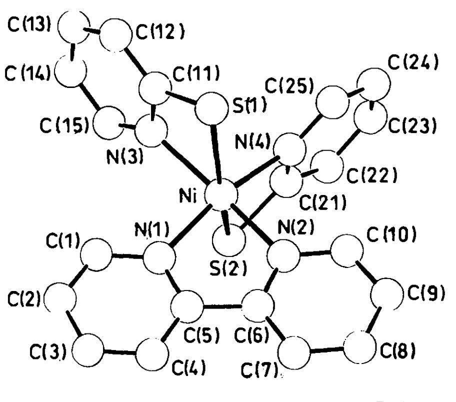

Figure. Molecular structure and labelling scheme for $[Ni(pyt)_2(bipy)]$

reported for Ni–N(bipy) in *cis*-bis(benzenethiolato)bis(2,2′-bipyridine)nickel(II) (2.088 Å),[21] and for Ni–N(pyt) in tetraethylammonium tris(pyridine-2-thionato)nickelate(II) (2.057 Å).[22] The fifth and sixth (axial) co-ordination sites around the nickel atom are occupied at greater distances by two sulphur atoms of the pyridine-2-thionato ligands with Ni–S(1) and Ni–S(2) bond distances of 2.475(2) and 2.495(1) Å respectively; these values do not differ significantly from the average Ni–S(pyt) distance observed in $[NEt_4][Ni(pyt)_3]$, 2.528(1) Å.[22]

The atoms of the equatorial region [N(1), N(2), N(3), and N(4)] deviate considerably from planarity. The *trans* equatorial atoms N(1) and N(4) are both below the best least-square plane (−0.5573 and −0.02302 Å), while N(2) and N(3) are above it (+0.7151 and +0.0724 Å), leading to N(1)–Ni–N(4) and N(2)–Ni–N(3) angles of 166.2(2) and 168.06(9)° respectively.

Further distortion is provided by the small bite of the pyridine-2-thionato ligands. This, in addition to the elongation in the axial direction, causes the S(1)–Ni–N(3) and S(2)–Ni–N(4) angles to be much smaller than 90°. The values observed are similar to those in other bidentate pyridine-2-thionato metal complexes.[22,23] The S(1)–Ni–S(2) angle is also distorted from 180 to 155.96(3)°.

The bipyridine ligand is essentially planar, with maximum carbon and nitrogen displacements of 0.06 Å. The pyridine portion of the pyridine-2-thionato ligands is planar, with the largest deviation from the best least-square planes being 0.009 Å and the deviations of the associated sulphur atoms being 0.003 for S(1) and 0.006 Å for S(2), so that these sulphur atoms are practically on the plane of the pyridine ring to which they are bound.

In the pyridine-2-thionato ligands the average N–C distance [1.347(4) Å] is smaller than in the free pyridine-2-thione ligand (1.39 Å), while the average S–C bond length of 1.728(3) Å is longer than that found in the free ligand, whose value of 1.68 Å has been considered as due to some double-bond character (*ca.* 65%) contributed by the thione form.[8] The C–C bond lengths are very similar. Together, these facts suggest that these ligands are closer to the pyridine-2-thionate than to the thione form.

The unco-ordinated bipyridine molecule in the crystal structure sits on a centre of symmetry and is planar, with *trans* arrangement about the inter-ring bond; it makes no significant contacts with the complex.

Vibrational Spectra.—The i.r. spectra are consistent with the structural data described above, but are otherwise not very informative. The spectra show that ν(NH) of the free pyridine-2-thione at 3 160 cm^{-1} (refs. 6 and 24) is absent for the metal complexes, suggesting that the hydrogen atom is lost during the electrochemical synthesis. The bands attributable to ring vibration at *ca.* 1 575, 1 540, 1 470, and 1 435 cm^{-1} indicate that the ligand is in the thiol form, as in di-2-pyridyl disulphide. The bands attributable to ring breathing vibration at *ca.* 1 005 and 630 cm^{-1} and the bands due to C–H bending at *ca.* 770 and 750 cm^{-1} are shifted to higher frequencies with respect to the corresponding disulphide bands, suggesting that the nitrogen atom is bound to the nickel(II) ion.[25] In addition, the mixed complexes exhibit i.r. absorptions typical of co-ordinated pyridine (650 and 440 cm^{-1}),[26] 1,10-phenanthroline (1 510, 850, and 725 cm^{-1}) and 2,2′-bipyridine (780 and 730 cm^{-1}).[27]

Electronic Absorption Spectra.—The electronic spectral data for the complexes are listed in Table 5. The electronic reflectance spectra of all the complexes are very similar and show bands in the 1 200—1 050 and 615—568 nm regions and a shoulder at *ca.* 950 nm. They are consistent with an octahedral environment around the nickel(II) ion[28] and can thus be assigned to transitions $^3A_{2g} \longrightarrow {}^3T_{2g}$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$. The shoulder on the low-energy side of the first band can be considered as the result of the splitting of the first band as a consequence of the low symmetry of the ligand field, and clearly indicates the distortion of octahedral symmetry in these complexes. This

Table 5. Electronic spectroscopic data for nickel(II) complexes

	Solid state $\lambda_{max.}$/nm	Solution $\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1}) dmf	MeOH
[Ni(pyt)$_2$]	615, 976, 1 200 (sh)	550 (38)	
[Ni(pyt)$_2$(bipy)]	583, 1 052, 1 190 (sh)	580 (48)	574 (42)
[Ni(pyt)$_2$(phen)]	568, 1 000, 1 170 (sh)	570 (41)	572 (43)
[Ni(pyt)$_2$(py)$_2$]	592, 1 070, 1 150 (sh)	588 (40)	

distortion is also reflected by higher values for the absorption coefficient (*ca.* 40 dm^3 mol^{-1} cm^{-1}) than are observed in regular octahedral systems, less than 30 dm^3 mol^{-1} cm^{-1}.[28] The third expected spin-allowed transition has not been observed, presumably due to the presence of a strong charge-transfer band in the 400—250 nm region.

The *X*-ray structure confirms the geometry of [Ni(pyt)$_2$(bipy)]·0.5 bipy and by implication the other complexes should also have highly distorted octahedral geometries. The complex [Ni(pyt)$_2$] is thus tentatively attributed a six-co-ordinated polymer structure with bidentate bridging pyt$^-$; at room temperature [Ni(pyt)$_2$] has a magnetic moment of 3.37 B.M. (B.M. $\approx$ 9.27 $\times$ 10^{-24} J T^{-1}), which is well within the range for octahedral complexes. In the case of the [Ni(pyt)$_2$(py)$_2$] complex the data are not sufficient to decide whether the two pyridine ligands are *cis* or *trans*.

The spectra of the complexes in solution are essentially the same as those in the solid state, suggesting that the complexes probably have the same structures in both states. The sole exception is [Ni(pyt)$_2$], which when dissolved in dimethylformamide turns from green to brown, with a resulting blue shift in *d–d* maxima.

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References

1 E. S. Raper, *Coord. Chem. Rev.*, 1985, **61**, 115 and refs. therein.
2 I. P. Evans and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1974, 946.
3 P. A. Lindahl, N. Kojima, R. P. Hausinger, J. A. Fox, B. K. Teo, C. T. Walsh, and W. H. Orme-Johnson, *J. Am. Chem. Soc.*, 1984, **106**, 3062.
4 R. A. Scott, S. A. Wallin, M. Czechowski, D. V. DerVartanian, J. LeGall, H. D. Peck, jun., and I. Moura, *J. Am. Chem. Soc.*, 1984, **106**, 6864.
5 M. K. Eidsness, R. J. Sullivan, and R. A. Scott, in 'The Bioinorganic Chemistry of Nickel,' ed. J. R. Lancaster, jun., VCH Publishers, New York, 1988, ch. 4.
6 E. Spinner, *J. Org. Chem.*, 1958, **23**, 2037; *J. Chem. Soc.*, 1960, 1237.
7 C. N. R. Rao, R. Venkataraghavan, and T. R. Kasturi, *Can. J. Chem.*, 1964, **42**, 36.
8 B. R. Penfold, *Acta Crystallogr.*, 1953, **6**, 707.
9 B. P. Kennedy and A. B. P. Lever, *Can. J. Chem.*, 1972, **50**, 3488; S. C. Kokkou, S. Fortier, P. J. Rentzeperis, and P. Karagiannidis, *Acta Crystallogr., Sect. C*, 1983, **39**, 178.
10 A. J. Deeming, M. N. Meah, H. M. Dawes, and M. B. Hursthouse, *J. Organomet. Chem.*, 1986, **299**, C25.
11 A. J. Deeming, K. J. Hardcastle, M. N. Meah, P. A. Bates, H. M. Dawes, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1988, 227.
12 P. Mura, B. G. Olby, and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1985, 2101.
13 S. R. Fletcher and A. C. Skaspki, *J. Chem. Soc., Dalton Trans.*, 1972, 635; M. Masaki, S. Matsunami, and H. Ueda, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3298.
14 J. D. Gilbert and G. Wilkinson, *J. Chem. Soc. A*, 1969, 1749; N. Lenhart and M. Singer, *Z. Naturforsch, Teil B.*, 1975, **30**, 284.
15 J. J. Habeeb, D. G. Tuck, and F. H. Walters, *J. Coord. Chem.*, 1978, **8**, 27.
16 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
17 W. H. Zachariasen, *Acta Crystallogr.*, 1963, **16**, 1139.
18 'International Tables for *X*-Ray Crystallography,' Birmingham, Kynoch Press, vol. IV, Table 2.2A, 1974 (present distributor D. Reidel, Dordrecht).
19 G. M. Sheldrick, SHELXS 86 Program for the Solution of Crystal Structures from Diffraction Data, University of Göttingen, 1986.
20 B. A. Frenz, The Enraf-Nonius CAD4 SPD, a Realtime System for Concurrent *X*-Ray Data Collection and Crystal Structure Determination, in 'Computing in Crystallography,' Delft University Press, 64—71; VAXSDP, Version 2.2, 1985.
21 K. Osakada, T. Yamamoto, A. Yamamoto, A. Takenaka, and Y. Sasada, *Acta Crystallogr., Sect. C*, 1984, **40**, 85.
22 S. G. Rosenfield, H. P. Berends, L. Gelmini, D. W. Stephan, and P. K. Mascharak, *Inorg. Chem.*, 1987, **26**, 2792.
23 S. G. Rosenfield, S. A. Swedberg, S. K. Arora, and P. K. Mascharak, *Inorg. Chem.*, 1986, **25**, 2109.
24 D. N. Sathyanarayana and S. V. K. Raja, *Spectrochim. Acta, Part A*, 1985, **41**, 809.
25 M. Masaki and S. Matsunami, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 3274.
26 N. S. Gill, R. H. Nutall, D. E. Scaiffe, and D. W. J. Sharp, *J. Inorg. Nucl. Chem.*, 1961, **18**, 79; D. P. Madden, M. M. daMota, and S. N. Nelson, *J. Chem. Soc. A*, 1970, 890.
27 A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, 1959, **9**, 211; R. G. Inskeep, *ibid.*, 1962, **24**, 763.
28 A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' 2nd edn., Elsevier, Amsterdam, 1984, p. 507.

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