Synthesis, Crystal and Molecular Structure and Magnetic Properties of $[Ni_3(L^1)_4(NCS)_4(OH)_2(OH_2)_2]$ (L^1 = 2,5-diamino-1,3,4-thiadiazole)[†]

Antonio C. Fabretti,[*,a] Wanda Malavasi,[a] Dante Gatteschi[*,b] and Roberta Sessoli[b]
[a] *Dipartimento di Chimica dell'Università, Via G. Campi, 183, 41100 Modena, Italy*
[b] *Dipartimento di Chimica dell'Università, Via Maragliano, 75, 50144 Firenze, Italy*

The product of the reaction between nickel(II) thiocyanate and 2,5-diamino-1,3,4-thiadiazole (L^1), $[Ni_3(L^1)_4(NCS)_4(OH)_2(OH_2)_2]$, has been characterized by means of structural, magnetic and spectroscopic measurements. The crystals are monoclinic, space group $P2_1/c$, with a = 8.132(2), b = 16.551(3), c = 12.495(2) Å, β = 95.52(1)° and Z = 2. The structure was solved by the heavy-atom method, and least-squares refinement of the structural parameters led to a conventional R factor of 0.034 for 1436 observed reflections. The structure consists of centrosymmetric trimeric discrete molecules in which the nickel(II) atoms are co-ordinated in slightly distorted octahedral geometries by two nitrogen atoms of the thiadiazoles, two nitrogen atoms of thiocyanate groups, and by two oxygen atoms. The central nickel atom is linked to each terminal nickel atom by two planar thiadiazole and one oxygen bridging molecule; the nearest-neighbour $Ni^{II}\cdots Ni^{II}$ distance is 3.320(4) Å.

1,3,4-Thiadiazoles have been investigated as versatile ligands which can yield mono- or poly-nuclear complexes.[1,2] In particular it was found that 1,3,4-thiadizaoles can behave either as monoco-ordinated ligands or as monoprotonated cations which involve hydrogen bonds with a highly condensed anion.[1,2] Similar molecules, 1,2,4-triazoles, can yield polynuclear metal complexes with interesting magnetic properties.[3–8] It was found that three 1,2,4-triazoles can bridge between two metal ions, yielding di- or tri-nuclear species.[7–10] In order to prevent such co-ordination and to favour the formation of thiocyanate bridges, Reedijk and co-workers[9] successfully used the strategy of employing bulky 3,5-disubstituted 1,2,4-triazoles. They were able to isolate a compound of formula $[Ni_3(L^2)_6(NCS)_6]\cdot 2H_2O$ (L^2 = 3,5-diethyl-1,2,4-triazole), in which the central and terminal nickel ions are bridged by two triazoles and one thiocyanate ion, while the terminal nickel ions complete their octahedral co-ordination with one triazole and two thiocyanate groups. We have found that using 2,5-diamino-1,3,4-thiadiazole, L^1, as a ligand a compound of formula $[Ni_3(L^1)_4(NCS)_4(OH)_2(OH_2)_2]$ is formed, which has two L^1 and one OH bridging groups between the central and terminal nickel ions. Herein we report its crystal structure and magnetic properties in order to compare them to those of $[Ni_3(L^2)_6(NCS)_6]\cdot 2H_2O$[9] and $[Ni_3(L^3)_6(NCS)_6]\cdot 6H_2O$[10] ($L^3$ = 3,5-diamino-1*H*-1,2,4-triazole). This compound also contains two pairs of metal ions bridged by two bidentate and one monodentate ligand, an arrangement which is widely found in a variety of systems. For instance iron atoms bridged by two carboxylates and an oxo or hydroxo group are known to be present in several metalloenzymes.[11,12]

Experimental

Nickel(II) thiocyanate and 2,5-diamino-1,3,4-thiadiazole were used as supplied commercially.

Synthesis.—The metal salt (1 mmol) dissolved in water (2 cm^3) was added to the ligand (3 mmol) also dissolved in water (6 cm^3). A very slow evaporation gave brown crystals suitable for X-ray data collection (Found: C, 15.45; H, 2.40; N, 29.85; S, 27.35. Calc. for $C_{12}H_{22}N_{20}Ni_3O_4S_8$: C, 15.30; H, 2.35; N, 29.70; S, 27.20%). Carbon, hydrogen, nitrogen and sulphur were determined with a Carlo Erba 1106 elemental analyser.

Spectral Measurements.—The IR spectra were recorded in the solid state with a Bruker 113r FT-IR spectrophotometer. Spectra in the range 4000–400 cm^{-1} were measured in KBr discs and in the range 400–50 cm^{-1} in polyethylene discs. Atmospheric water was removed by flushing with dry nitrogen. The electronic spectrum was recorded with a Perkin-Elmer Lambda 9 spectrometer.

Magnetic Susceptibility Measurements.—Magnetic susceptibilities were measured in the range 4.2–300 K with a fully automated AZTEC DSM5 susceptometer equipped with an Oxford Instruments CF 1200S continuous flow cryostat and a Bruker BE15 electromagnet, operating at *ca.* 1.21(4) T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal's constants.

Crystallography.—*Crystal data.* $C_{12}H_{22}N_{20}Ni_3O_4S_8$, M = 943.05, monoclinic, space group $P2_1/c$ (no. 14), a = 8.132(2), b = 16.551(3), c = 12.495(2) Å, β = 95.52(1)°, U = 1673.98 Å^3, Z = 2, D_c = 1.85 (D_m = 1.87 by flotation) g cm^{-3}, $F(000)$ = 956, graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 2.12 mm^{-1}, crystal dimensions *ca.* 0.2 × 0.2 × 0.2 mm. Unit cell parameters were derived from least-squares fitting to the setting angles of 25 intense reflections in the range θ 8–16°.

The intensity data were collected at room temperature on a CAD 4 Enraf-Nonius automatic diffractometer with the ω–2θ scan technique in the range 2–26°, max. sin(θ/λ) 0.61 Å^{-1}, at a scan speed range of 1.5–5.5° min^{-1}, with a scan width (1.0 + 0.35 tan θ)°. Reflections measured: $\pm h$, k, l. Two standard reflections were measured every 2 h, and the intensities showed no significant changes. 3557 Reflections were collected of which

---

[†] Diaqua-1κ*O*, 3κ*O*-tetrakis(μ-2,5-diamino-1,3,4-thiadiazole)-1:2-κ^2-N^3:N^4; 1:2-κ^2N^3:N^4; 2:3-κ^2-N^3:N^4; 2:3-κ^2N^3:N^4-di-μ-hydroxo-1:2-κ^2O; 2:3-κ^2O-tetrathiacyanato-1κ^2N, 3κ^2N-trinickel(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

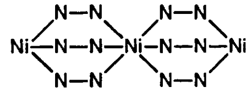
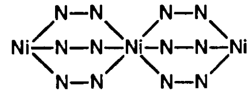
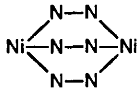
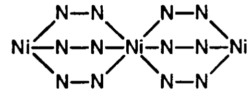
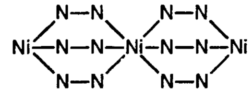
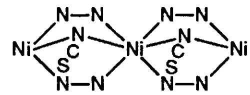
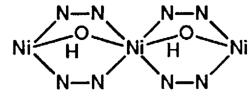
Table 1 Fractional atomic coordinates for $[Ni_3(L^1)_4(NCS)_4(OH)_2(OH_2)_2]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni(1)	0.0	0.0	0.0
Ni(2)	0.1974(1)	0.113 87(5)	0.189 88(7)
O(1)	−0.0180(5)	0.0954(2)	0.1023(3)
O(2)	0.0701(6)	0.1326(3)	0.3311(4)
S(1)	0.1724(2)	−0.1564(1)	0.2953(2)
S(2)	0.4730(3)	0.1094(1)	−0.1173(2)
S(3)	0.7045(2)	0.1714(1)	0.4103(2)
S(4)	0.2438(4)	0.3892(2)	0.0736(2)
N(1)	0.0948(6)	−0.0593(3)	0.1391(4)
N(2)	0.1895(6)	−0.0137(3)	0.2177(4)
N(3)	−0.0171(8)	−0.1889(3)	0.1112(5)
N(4)	0.3308(9)	−0.0292(4)	0.3899(5)
N(5)	0.3201(7)	0.0959(3)	0.0515(4)
N(6)	−0.2425(6)	−0.0421(3)	0.0233(4)
N(7)	0.2609(8)	−0.0057(4)	−0.1973(5)
N(8)	0.5465(8)	0.1875(4)	0.0716(5)
N(9)	0.4123(8)	0.1314(3)	0.2890(5)
N(10)	0.1865(8)	0.2367(4)	0.1574(5)
C(1)	0.2378(9)	−0.0559(4)	0.3028(6)
C(2)	0.0740(8)	−0.1332(4)	0.1685(5)
C(3)	0.4420(9)	0.1343(4)	0.0140(6)
C(4)	0.3089(9)	0.0416(4)	−0.1141(6)
C(5)	0.5324(9)	0.1477(4)	0.3400(6)
C(6)	0.211(1)	0.2999(5)	0.1226(6)

Table 2 Bond lengths (Å) and angles (°) for $[Ni(L^1)_4(NCS)_4(OH)_2(OH_2)_2]$

Ni(1)–N(1)	2.080(5)	C(4)–N(7)	1.330(9)
Ni(2)–O(1)	1.997(4)	C(6)–N(10)	1.158(9)
Ni(2)–N(5)	2.099(5)	C(2)–S(1)	1.746(7)
C(1)–S(1)	1.747(7)	C(5)–S(3)	1.628(8)
C(4)–S(2)	1.745(8)	C(2)–N(1)	1.293(8)
N(1)–N(2)	1.406(7)	C(1)–N(4)	1.340(8)
C(2)–N(3)	1.341(8)	C(3)–N(8)	1.375(9)
Ni(1)–N(6)	2.138(5)	C(3)–S(2)	1.735(7)
Ni(2)–O(2)	2.153(5)	C(6)–S(4)	1.633(8)
Ni(2)–N(9)	2.064(6)	C(1)–N(2)	1.300(8)
Ni(1)–O(1)	2.047(4)	C(3)–N(5)	1.301(8)
Ni(2)–N(2)	2.143(5)	C(5)–N(9)	1.145(8)
Ni(2)–N(10)	2.072(6)		
N(1)–Ni(1)–O(1)	83.4(2)	N(6)–Ni(1)–O(1)	92.5(2)
N(6)–Ni(1)–N(1)	90.3(2)	O(2)–Ni(2)–O(1)	90.3(2)
N(2)–Ni(2)–O(1)	84.3(2)	N(2)–Ni(2)–O(2)	89.1(2)
N(5)–Ni(2)–O(1)	89.4(2)	N(5)–Ni(2)–O(2)	179.6(1)
N(5)–Ni(2)–N(2)	91.0(2)	N(9)–Ni(2)–O(1)	176.3(2)
N(9)–Ni(2)–O(2)	86.2(2)	N(9)–Ni(2)–N(2)	94.5(2)
N(9)–Ni(2)–N(5)	94.1(2)	N(10)–Ni(2)–O(1)	91.4(2)
N(10)–Ni(2)–O(2)	90.2(2)	N(10)–Ni(2)–N(2)	175.6(2)
N(10)–Ni(2)–N(5)	89.6(2)	N(10)–Ni(2)–N(9)	89.8(2)
Ni(2)–O(1)–Ni(1)	110.4(2)	C(2)–S(1)–C(1)	87.1(3)
C(4)–S(2)–C(3)	87.1(3)	N(2)–N(1)–Ni(1)	117.6(4)
C(2)–N(1)–Ni(1)	129.6(5)	C(2)–N(1)–N(2)	112.7(5)
N(1)–N(2)–Ni(2)	116.0(3)	C(1)–N(2)–Ni(2)	130.5(4)
C(1)–N(2)–N(1)	112.7(5)	C(3)–N(5)–Ni(2)	131.7(5)
C(5)–N(9)–Ni(2)	173.9(6)	C(6)–N(10)–Ni(2)	162.7(7)
N(2)–C(1)–S(1)	113.6(5)	N(4)–C(1)–S(1)	120.1(5)
N(4)–C(1)–N(2)	126.3(6)	N(1)–C(2)–S(1)	113.9(5)
N(3)–C(2)–S(1)	121.1(5)	N(3)–C(2)–N(1)	125.0(6)
N(5)–C(3)–S(2)	114.2(5)	N(8)–C(3)–S(2)	120.5(5)
N(8)–C(3)–N(5)	125.2(6)	N(7)–C(4)–S(2)	121.9(6)
N(9)–C(5)–S(3)	179.0(7)	N(10)–C(6)–S(4)	179.8(2)

Table 3 Calculated *J* values

Compound	Bonding scheme	*J*/cm^{-1}	Ref.
$[Ni_3(L^4)_6(H_2O)_6]^{6+}$		18.8	17
$[Ni_3(L^5)_8(NCS)_4]^{2+}$		20	18
$[Ni_2(L^6)_4(NCS)_4(H_2O)]$		17.4	19
$[Ni_3(L^7)_{12}]^{6+}$		14	20
$[Ni_3(L^3)_6(NCS)_6]$		10	10
$[Ni_3(L^2)_6(NCS)_6]$		−20	9
$[Ni_3(L^1)_4(NCS)_4(OH)_2(OH_2)_2]$		10	This work

L^4 = 4-Ethyl-, L^5 = 4-*tert*-butyl-, L^6 = 4-allyl- and L^7 = 4-*tert*-butyl-3-methyl-1,2,4-triazole.

1506 with $I > 3.0\ \sigma(I)$ were observed and 1436 were unique (after merge $R_{int} = 0.022$). The unique reflections were used in the refinement; number of parameters 214; $\Delta\rho = -0.3$ to 0.4 e Å^{-3}.

All data were corrected for Lorentz and polarization effects and an empirical absorption correction, based on Ψ scans, was applied[13] (max., min. transmission factor = 0.99, 0.96). The structure was solved by Patterson and Fourier methods, and refined by full-matrix least-squares calculations minimizing $\Sigma w(|F_o| - |F_c|)^2$.

Non-hydrogen atoms were treated anisotropically, whereas the hydrogen atoms were treated as fixed contributors at located positions from difference Fourier maps, assuming a thermal parameter Å^2 greater than that of the attached nitrogen atoms; the N–H bond lengths and angles so determined are reasonable.

This model converged to $R = 0.034$ and $R' = 0.034$, $w = 1.1/[\sigma^2(F) + 0.0003F_o^2]$. During refinement zero weights were assigned to ten low-order reflections, which may be affected by secondary extinction.

Complex neutral-atom scattering factors[14] were employed throughout; major calculations were carried out on a Vax 6210 computer, using the SHELX 76[15] program package and the ORTEP[16] plotting program. Final fractional coordinates for non-hydrogen atoms are given in Table 1. Bond distances and angles are given in Table 2. The calculated value of *J* compared to those of analogous compounds with differing bridging ligands is reported in Table 3.

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

Results and Discussion

Crystal Structure.—The structure of $[Ni_3(L^2)_4(NCS)_4(OH)_2(OH_2)_2]$ consists of discrete trimeric, centrosymmetric, molecules, Fig. 1. One of the two crystallographically independent nickel atoms is in a special position, and each nickel atom shows a slightly distorted octahedral co-ordination geometry.

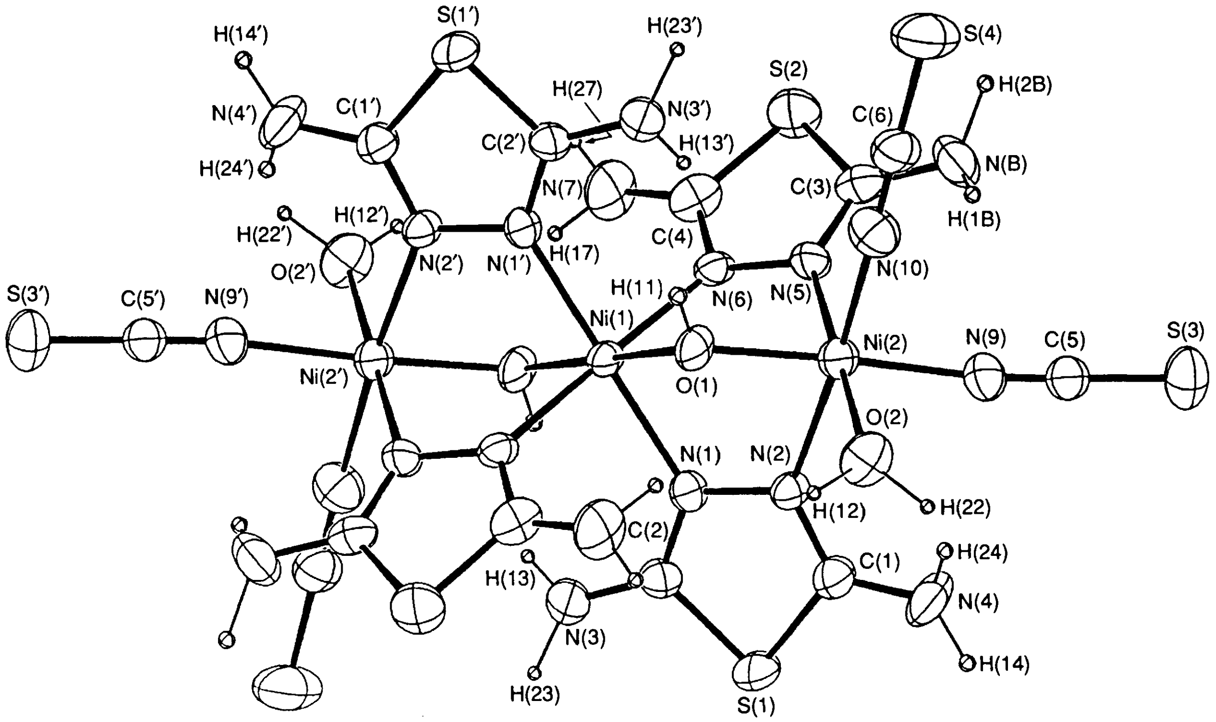


Fig. 1 ORTEP view of $[Ni_3(L^1)_4(NCS)_4(OH)_2(OH_2)_2]$ showing the atom numbering and thermal ellipsoids (50%) for the non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius

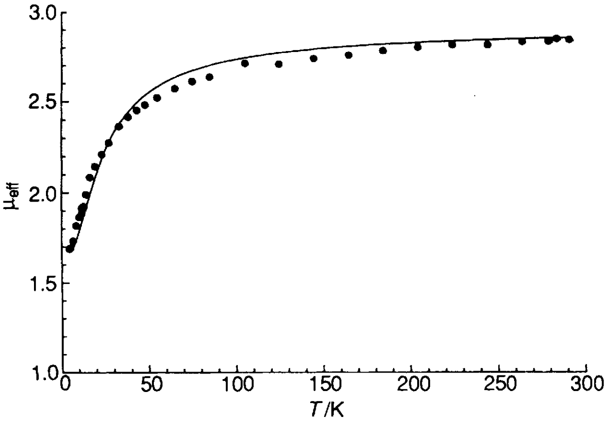


Fig. 2 Temperature dependence of μ_{eff}. The solid line represents the best fit (see text)

The central nickel atom is co-ordinated by four N (thiadiazole) and two oxygen atoms while the terminal nickel atoms are co-ordinated by two N (thiadiazole), two N (thiocyanate) and two oxygen atoms. Two ligands L^1 and one oxygen atom bridge the central and terminal nickel ions (the presence of the hydroxy bridge is a normal feature in metal-ion hydrolysis). The four unique Ni–N (thiadiazole) bond distances [2.080(5), 2.138(5), 2.143(5) and 2.099(5) Å] are slightly different from each other but are very close to values found in the literature: 2.127(3) and 2.093(3) Å in $[Ni_3(L^3)_6(NCS)_6]\cdot 6H_2O$,[10] 2.052(3)–2.112(3) Å in $[\{Ni(C_2H_3N_3)(H_2O)_3\}_2(NO_3)_6(H_2O)_2]$[5] and 2.10(1) Å in $[Ni_3(L^2)_6(NCS)_6]\cdot 2H_2O$.[8]

The distortion from ideal octahedral geometry of the co-ordination polyhedra involves both the dihedral angles between planes and the bond angles; deviations from ideal values are smaller around the terminal Ni atoms (max. 3.0 and 3.7°) than around the central metal atom (max. 6.6 and 6.4°). The nickel atoms are displaced from the mean plane through the thiadiazole rings by 0.062, 0.114 Å and 0.319, 0.024 Å for Ni(1) and Ni(2) respectively.

The nearest-neighbour $Ni^{II}\cdots Ni^{II}$ distance within the trimeric molecule is 3.320(4) Å, close to the separation of 3.39(1) Å observed in $[Ni_3(L^2)_6(NCS)_6]\cdot 2H_2O$[8] in which two triazole and one thiocyanate group bridge two nickel atoms.

One of the two unique thiadiazole rings is found to be planar within experimental error, while the other shows slight distortion. Bond distances and angles of the ring compare well with those found by other workers.[21–24]

Intermolecular hydrogen-bond contacts, on which the crystal packing mainly depends, occur between the NH_2 groups and the sulphur atom of the thiocyanate groups, and the oxygen atoms; in particular strong interactions occur between the hydroxo and amino groups, with $O\cdots N$ separations of 2.823 and 3.087 Å, and $O\cdots H$ separations of 1.956 and 2.116 Å, respectively, with subtended OHN angles of 145.5 and 155.4°, respectively. Intramolecular hydrogen-bond contacts occur between the nitrogen and sulphur atoms of the thiocyanate groups, and the NH_2 groups.

Magnetic Properties.—The temperature dependence of the effective magnetic moment for $[Ni_3(L^1)_4(NCS)_4(OH)_2(OH_2)_2]$ in the range 4–300 K is shown in Fig. 2. The observed decrease of μ_{eff} with decreasing temperature is a clear indication of dominant antiferromagnetic interactions within the trinuclear units, as observed previously for triazole-bridged nickel(II) complexes. The experimental data can be fitted to a spin Hamiltonian which includes only nearest-neighbour magnetic interaction. The best-fit parameters are $g = 2.07(1)$ and $J = 10.0(4)$ cm^{-1}. The unusually low value of the g factor is probably due to zero-field splitting effects which were not taken into account.

The calculated value of J is compared to previously reported values for analogous bridging ligands in Table 3. It is apparent that in all the complexes with three triazole bridges the coupling is antiferromagnetic with J ranging from 10 to 20 cm^{-1}. In the two reported cases with two triazole bridges and an exogenous bridge, J was found to be ferromagnetic with NCS^- but antiferromagnetic with OH^-. The similarity of the value of J observed here and that of the three-bridged complexes suggests that for nickel(II) OH^- is roughly as effective as triazole in transmitting the exchange interaction. In fact *J* values of *ca.* 18 cm^{-1} were reported for methoxo bridged nickel(II) complexes.[25]

Spectroscopic Properties.—The presence of OH and OH_2 co-ordinated species complicates the interpretation of the IR spectrum of $[Ni_3(L^1)_4(NCS)_4(OH)_2(OH_2)_2]$. An OH band is observed at 3633m cm^{-1}, and the characteristic bridging OH bending mode near 1000 cm^{-1} is obscured by the presence of ligand bands. The fact that the NCS groups are co-ordinated *via* the nitrogen atoms as monodentate ligands and that they are *cis* to each other is established by observations of a doublet at 2098vs and 2117vs cm^{-1}. In the far-IR spectrum, three new bands with respect to the free ligand molecule spectrum are found at 402m, 280m and 245s cm^{-1}. The bands below 300 cm^{-1} can be assigned as being primarily due to Ni–N(thiocyanate) stretching modes while that near 400 cm^{-1} can be assigned to the Ni–O stretching mode.[26]

The ligand-field spectrum [10 000, 15 000 (sh) and 16 550 cm^{-1}] is in agreement with octahedral co-ordination geometry for this metal ion.[9]

Acknowledgements

We are grateful to the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) of Italy for grants, to the Centro Interdipartimentale di Calcolo Automatico ed Informatica Applicata (CICAIA) of Modena University for computer facilities, and to the Centro Interdipartimentale Grandi Strumenti of Modena University for the recording of spectra and intensity data collection.

References

1 L. Antolini, A. Benedetti, A. C. Fabretti, A. Giusti and M. C. Menziani, *J. Chem. Soc., Dalton Trans.*, 1988, 1075.
2 L. Antolini, A. Benedetti, A. C. Fabretti and A. Giusti, *J. Chem. Soc., Dalton Trans.*, 1988, 2501.
3 J. A. Jarvis, *Acta Crystallogr.*, 1962, **15**, 964.
4 M. Inoue and M. Kubo, *Coord. Chem. Rev.*, 1976, **21**, 1.
5 D. W. Engelfriet, W. L. Groeneveld, H. A. Groenendijk, J. J. Smit and G. M. Nap, *Z. Naturforsch., Teil A*, 1980, **35**, 115.
6 C. W. Reimann and M. Zocchi, *Acta Crystallogr., Sect. B*, 1971, **27**, 682.
7 G. Vos, R. A. le Febre, R. A. G. de Graaff, J. G. Haasnoot and J. Reedijk, *J. Am. Chem. Soc.*, 1983, **105**, 1682.
8 R. Prins, R. A. G. de Graaff, J. G. Haasnoot, C. Vader and J. Reedijk, *J. Chem. Soc., Chem. Commun.*, 1986, 1430.
9 G. A. van Albada, R. A. G. de Graaff, J. G. Haasnoot and J. Reedijk, *Inorg. Chem.*, 1984, **23**, 1404.
10 L. Antolini, A. C. Fabretti, D. Gatteschi, A. Giusti and R. Sessoli, *Inorg. Chem.*, 1990, **29**, 143.
11 R. E. Stenkamp, L. C. Sieker and L. H. Jensen, *J. Am. Chem. Soc.*, 1984, **106**, 618.
12 S. Sheriff, W. A. Hendrickson and J. L. Smith, *Life Chem. Rep.*, 1983, Suppl. 1305.
13 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
14 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, p. 174.
15 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University Chemical Laboratory, Cambridge, 1976.
16 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
17 G. Vos, J. G. Haasnoot, G. C. Verschoor, J. Reedijk and P. E. L. Schaminee, *Inorg. Chim. Acta*, 1985, **105**, 31.
18 L. R. Groeneveld, R. A. le Febre, R. A. G. de Graaff, J. G. Haasnoot, G. Vos and J. Reedijk, *Inorg. Chim. Acta*, 1985, **102**, 69.
19 G. Vos, J. G. Haasnoot, G. C. Verschoor and J. Reedijk, *Inorg. Chim. Acta*, 1985, **102**, 187.
20 W. Vreugdenhil, J. G. Haasnoot, M. F. J. Schoondergang and J. Reedijk, *Inorg. Chim. Acta*, 1987, **130**, 235.
21 D. W. Engelfriet, W. Den Brinker, G. C. Verschoor and S. Gorter, *Acta Crystallogr., Sect. B*, 1979, **35**, 2922.
22 L. Pauling, *The Nature of the Chemical Bond*, 3rd edn., Cornell University Press, Ithaca, New York, 1960.
23 H. Senda, H. Matsuoka and J. Maruha, *Acta Crystallogr., Sect. C*, 1986, **42**, 1087.
24 H. Toyofuku, H. Nagasawa, Y. Ohtake, S. Sawaki and T. Kuroda, *Acta Crystallogr., Sect. C*, 1987, **43**, 1846.
25 W. L. Gladfelter, M. W. Lynch, W. P. Schaefer, D. N. Hendrickson and H. B. Gray, *Inorg. Chem.*, 1981, **20**, 2390.
26 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1986.

Received 5th *February* 1991; *Paper* 1/00546D