Pergamon

PII: S0277-5387(97)00014-4

Polyhedron Vol. 16, No. 16, pp. 2863–2869, 1997
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0277–5387/97 \$17.00+0.00

Synthesis, crystal structure and equilibrium studies on bidentate amine adducts of bis(S-benzyl)-β-N-(4-dimethylaminobenzyl) methylendithiocarbazone nickel(II) complex

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(Received 30 July 1996; accepted 12 December 1996)

Abstract—The novel adducts of chelating diamines to the diamagnetic, square-planar nickel(II) complex bis(S-benzyl)-β-N-(4-dimethylaminobenzyl)methylendithiocarbazone nickel(II) [hereafter abbreviated $Ni(SN)_2$] have been prepared and characterized, where the chelating diamines are 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy), 5-nitro-1,10-phenanthroline (NO_2phen), 4,4′-methyl-2,2′-bipyridine (Mebipy) and 4,5-diazafluren-9-one (diafo). The addition equilibrium constants (K), determined by a UV–vis spectrometer, were influenced by the coordinating ability of the added ligands in the order: $K_{\text{phen}} > K_{\text{mebipy}} > K_{\text{bipy}} > K_{\text{NO}_2\text{phen}} > K_{\text{diafo}}$. The single crystal structure of the phenanthroline adduct was determined to study the possible mechanism of the addition processes. The coordination geometry of the nickel atom is distorted octahedral. The four nitrogen atoms of the two SN ligands and the phenanthroline molecule form the equatorial plane with a Ni—N distance *ca* 2.10 Å and the two sulfur atoms site at the axial positions with the Ni—S distance of 2.40 Å. From the results of structural determination and the addition equilibrium studies, the possible addition mechanisms have been discussed. © 1997 Elsevier Science Ltd

Keywords: crystal structure; adducts; nickel(II) complexes; dithiocarbazone; addition mechanism; synthesis.

The coordination number of the low-spin square-planar nickel(II) complexes can often be increased by the addition of the other ligands to form high-spin octahedral nickel(II) complexes with donor ligands containing nitrogen and sulfur, such as xanthates (R_2NCS_2) [1–4], and dithiophosphates [$(RO)_2PS_2$] [5–7]. Recently, metal complexes with Schiff-base ligands containing nitrogen and sulfur as donors and their bidentate amine adducts received much attention in our laboratory, due to their wide use in nonlinear optical materials [8–10]. In this paper, we report the synthesis, crystal structure and the addition equilibrium studies of bidentate amines to the square-planar nickel(II) complex.

EXPERIMENTAL

Physical measurements

Elemental analyses were performed on a Perkin–Elmer 240 analytical instrument. IR spectra were recorded on a Nicolet FTIR170SX instrument (KBr discs) in the 4000–400 cm^{-1} range. The far-IR spectra were recorded as Nujol mulls between polyethylene sheets in the 500–100 cm^{-1} range. Electronic spectra were obtained on a Shimadzu 240 spectrophotometer in CH_2Cl_2 solution. The solid-state electronic spectra were measured by the reflectance technique on a Shimadzu 240 spectrophotometer using MgO as a reflectance material. Magnetic measurement on a powder sample was carried out with a CAHN 2000 Faraday-

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type magnetometer in the temperature range 75–300 K.

Preparations

Solvents were purified by conventional methods; bidentate amines excepted diafo were dried *in vacuo* at 70°C. All other chemicals were of analytical grade without further purification. The parent nickel(II) complex [11] and the diafo [12] were prepared according to the literature method.

The adducts [NiL(SN)$_2$] were prepared by dissolving the parent nickel complex (0.72 g, 1 mmol) and bidentate amine (4 mmol) in CH_2Cl_2 (30 cm^3). After refluxing for 1 h, the mixture was evaporated to dryness and was washed with EtOH. Crystals suitable for X-ray structure determination of the phenanthroline adduct were formed by slowly evaporating a CH_2Cl_2 solution of the adduct. Analytical data and relevant IR frequencies (cm^{-1}) as well as the electronic spectra data of those adducts are given in Table 1.

X-ray crystal structure determination of Ni(phen)(SN)$_2$

The relevant crystal data and structural parameters are summarized in Table 2. The intensities were collected at 294 K on a Rigaku RAXIS-IIC imaging plate diffractometer using Mo-K_α (λ = 0.71073 Å) from a rotating-anode generator operating at 50 KV and 90 mA ($2\theta_{max}$ = 55.2°); 60 oscillation frames in the range 0–180° exposure 8 min per frame for the complex [13,14].

The structure was solved by direct methods. All non-hydrogen atoms were refined anistropically by full-matrix least squares. Hydrogen atoms were placed in their calculated position with C—H = 0.96 Å, assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculations.

Table 2. Crystal data for [Ni(phen)(SN)$_2$]

Complex	[Ni(phen)(SN)$_2$]
Formula	$C_{46}H_{44}N_8S_4Ni$
Colour/habit	Dark-brown prism
Size (mm)	0.14 × 0.28 × 0.32
Space group	$P\bar{1}$
a (Å)	11.608(2)
b (Å)	12.872(3)
c (Å)	17.618(4)
α (°)	75.73(3)
β (°)	72.89(3)
γ (°)	63.34(3)
V (Å^3)	2228.3(11)
Z	2
D_{calc} (g cm^{-3})	1.338
μ (mm^{-1})	0.665
Formula weight	897.9
F(000)	940
Reflection unique	6946
Data used in refinement	3000
Final R, R_w	0.058, 0.089
$\Delta(\rho)_{max, min}$ (e Å^{-3})	0.71, −0.39

All calculations were carried out on a PC-486 computer using the SHELXTL-PC program package [15]. Analytical expressions of neutral-atom scattering factor were employed and anomalous dispersion corrections were incorporated [16]. Selected bonds lengths and angles for the title complexes are listed in Table 3.

Additional materials available from the Cambridge Crystallographic Data Center comprise complete lists of atomic coordinates, thermal parameters and bond lengths and angles.

Equilibrium studies

Addition of bidentate amines to a CH_2Cl_2 solution of [Ni(SN)$_2$] results in a complex series of spectral

Table 1. Selected IR data, elemental analysis and electronic spectra data

					Analytic data				
Compound	IR data			C	H	N	UV–vis data		
NiL$^1_2$	944	455	371	57.1	5.31	11.8	452	674	
				(56.9)	(5.1)	(11.7)	(4.66)	(2.7)	
Ni(phen)(SN)$_2$	926	433	351	60.4	5.0	12.3	452	388	880
				(61.6)	(4.9)	(12.5)	(3.12)	(4.89)	(3.04)
Ni(NO$_2$phen)(SN)$_2$	927	432	354	58.6	4.5	13.5	452	388	880
				(58.7)	(4.6)	(13.4)	(3.24)	(4.78)	(3.02)
Ni(bipy)(SN)$_2$	935	435	355	60.6	5.0	12.8	452	388	880
				(60.0)	(5.0)	(12.9)	(4.19)	(4.53)	(3.03)
Ni(Me$_2$bipy)(SN)$_2$	942	431	359	61.5	5.1	12.4	452	388	880
				(61.4)	(5.4)	(12.5)	(3.52)	(4.65)	(3.01)

Table 3. Selected bond lengths (Å) and angles (°)

Ni(1)—S(1)	2.419(1)	Ni(1)—S(3)	2.403(1)
Ni(1)—N(5)	2.107(2)	Ni(1)—N(2)	2.105(2)
Ni(1)—N(7)	2.098(2)	Ni(1)—N(8)	2.102(2)
S(1)—C(1)	1.718(2)	S(3)—C(18)	1.702(2)
N(1)—N(2)	1.395(2)	N(1)—C(1)	1.283(2)
N(2)—C(2)	1.284(1)	N(4)—C(18)	1.299(2)
N(4)—N(5)	1.398(1)	N(5)—C(19)	1.295(2)
S(1)—Ni(1)—S(3)	179.0(1)	S(1)—Ni(1)—N(2)	81.6(1)
S(3)—Ni(1)—N(2)	97.1(1)	S(1)—Ni(1)—N(5)	97.6(1)
S(3)—Ni(1)—N(5)	81.7(1)	N(2)—Ni(1)—N(5)	93.0(1)
S(1)—Ni(1)—N(7)	89.3(1)	S(3)—Ni(1)—N(7)	170.1(1)
N(2)—Ni(1)—N(7)	95.0(1)	N(5)—Ni(1)—N(7)	170.1(1)
S(1)—Ni(1)—N(8)	87.9(1)	S(3)—Ni(1)—N(8)	92.8(1)
N(2)—Ni(1)—N(8)	167.7(1)	N(5)—Ni(1)—N(8)	94.7(1)
N(7)—Ni(1)—N(8)	78.5(1)	Ni(1)—N(2)—N(1)	119.6(1)
Ni(1)—S(3)—C(18)	94.2(5)	Ni(1)—S(1)—C(1)	93.9(1)
N(2)—N(1)—C(1)	115.4(1)	N(5)—N(4)—C(18)	113.4(1)
Ni(1)—N(5)—N(4)	120.3(1)	Ni(1)—N(7)—C(46)	113.6(1)
Ni(1)—N(8)—C(45)	113.2(1)		

changes (Figure 1). In all cases, it was found that binding of the diamine is fast, so that no incubation of the mixtures was necessary before the spectroscopic measurement. Intensity measurements were taken at the wavelength of *ca* 450 nm. Addition equilibrium constants were calculated by the method of Benesi-Hidebrad [17].

RESULTS AND DISCUSSION

Synthesis and characterization

Table 1 shows the elemental analysis data, IR spectra and electronic spectra data. The new bands at *ca* 1400 cm^{-1} are a characterization of ν(C=N) and ν(C=C) in the chelating diamine ligand. Still, there are small but obviously red shifts of the metal–ligand vibrations compared with that of the parent nickel(II) complex such as the ν(M—S) from *ca* 370 cm^{-1} to the lower frequency at *ca* 350 cm^{-1}. It may be demonstrated that the increase of the coordination number reduces the strength of the coordinated bond. The electronic spectra give other proof of the existence of the chelating diamines and increase of coordinated number. The new bands at *ca* 388 nm might be the strong $\pi \rightarrow \pi$ transition of the chelating diamines. The $d \rightarrow d$ band at *ca* 880 nm rather than 670 nm of the parent complex might be taken as an evidence for the six-coordinated octahedral nickel(II) complexes, while the parent four-coordinated nickel(II) complexes always show the $d \rightarrow d$ bands at 670 nm [11]. The magnetic moment of the adducts are 3.0 ± 0.1 B.M., typical of octahedral nickel(II) complexes, while that of the parent complex is diamagnetic.

Single crystal structure of the phenanthroline adduct

Figure 2 shows an ORTEP drawing of the Ni(phen)$(SN)_2$ with the atom numbering scheme. The coordination geometry of nickel(II) is a distorted octahedron. The four nitrogen atoms, N(1), N(2) of the phenanthroline and N(3), N(6) from the Schiff-base ligand with the bond lengths *ca* 2.10 Å form the equatorial plane (mean deviation from plane = 0.040 Å), while the two sulfur atoms S(1) and S(3) are fixed on the axial positions. This structure is quite useful for determining the possible mechanism of the adductive process. As can be expected, the addition of the bidentate amine might weaken the original coordinated bonds [18,19]. This exception is supported by the slight but significant lengthening of the Ni—S bonds (2.40 Å, average of the phenanthroline adduct *vs* 2.18 Å, average of the parent complex [11]) and Ni—N bonds (2.10 Å average *vs* 1.92 Å [11]).

Addition equilibrium studies

The addition equilibrium studies are taken in the dichloromethane solution by adding the adductive ligands to the parent complex. The intensity measurements were taken at the wavelengths 452, 432 and 490 nm, respectively. By the formula of Benesi-Hildebrad [15] the adductive equilibrium constants obtained are listed in Table 4. It is very obvious to see that the adductive constants were decreased by electron-withdrawing in the adduct ligand, such as an NO_2 group, and increased by the electron-donor substitutes in the adduct ligand, such as the CH_3 group. For the five bidentate amines there are the orders $K_{\text{phen}} > K_{\text{mebipy}} > K_{\text{bipy}} > K_{\text{NO}_2\text{phen}} > K_{\text{diafo}}$. Indeed, there is no

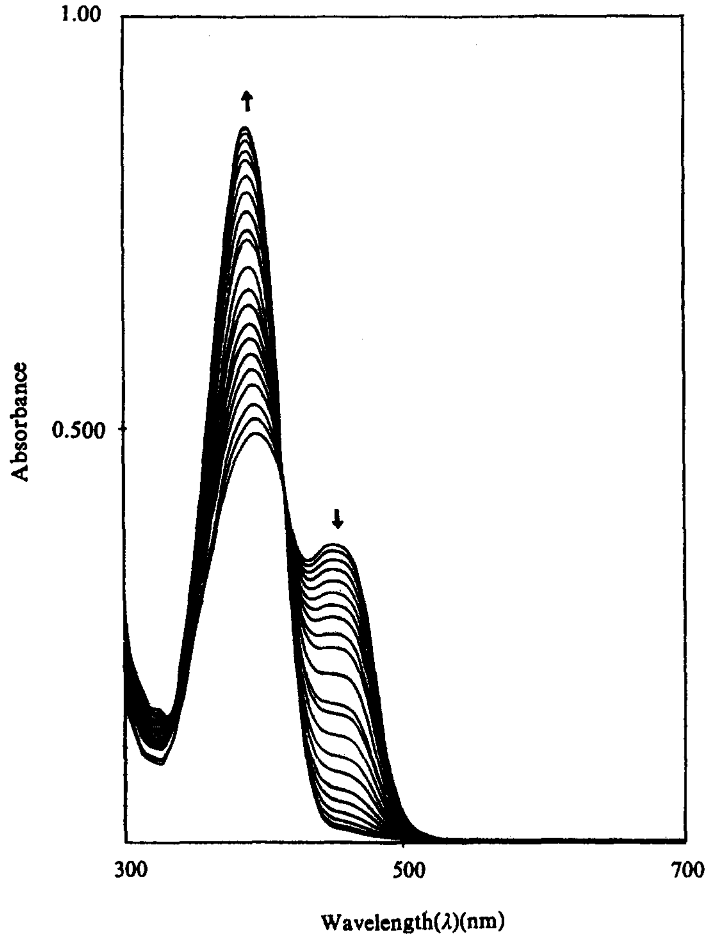


Fig. 1. Spectral changes in the course of phenanthroline addition to $Ni(SN)_2$ in CH_2Cl_2 solution (2×10^{-5} mol dm^3 m) at 298K.

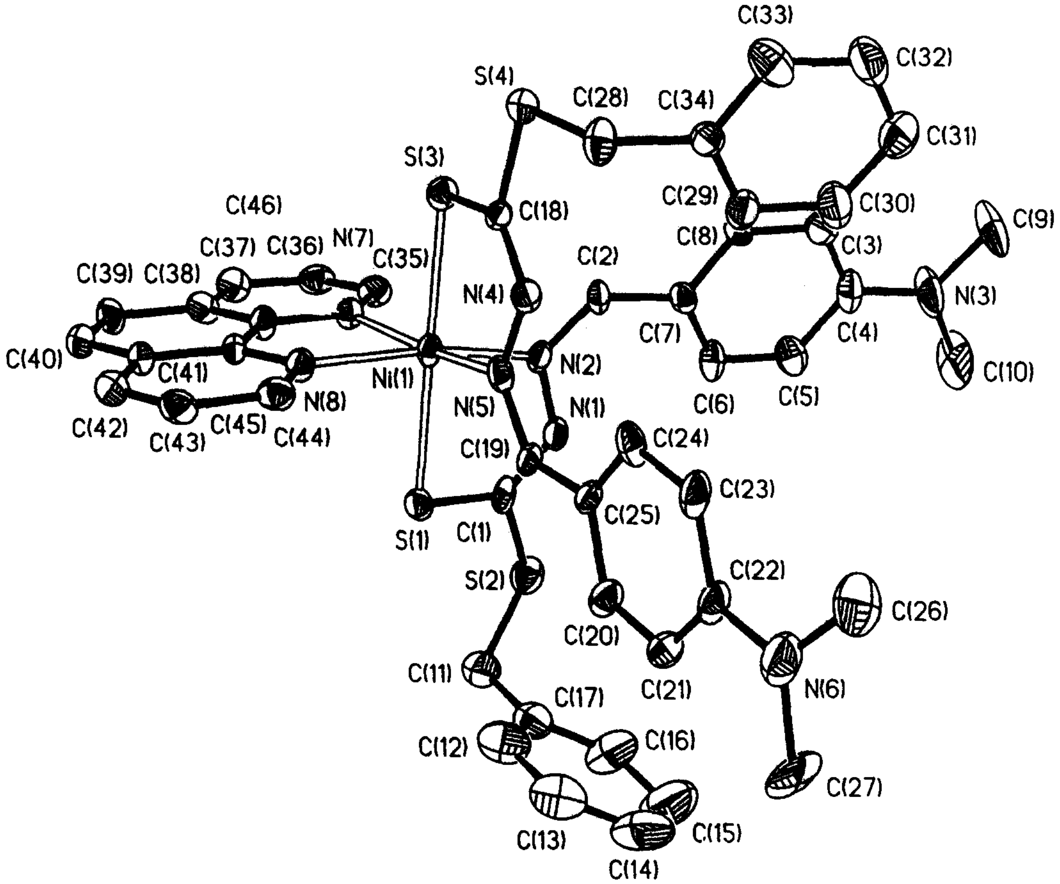
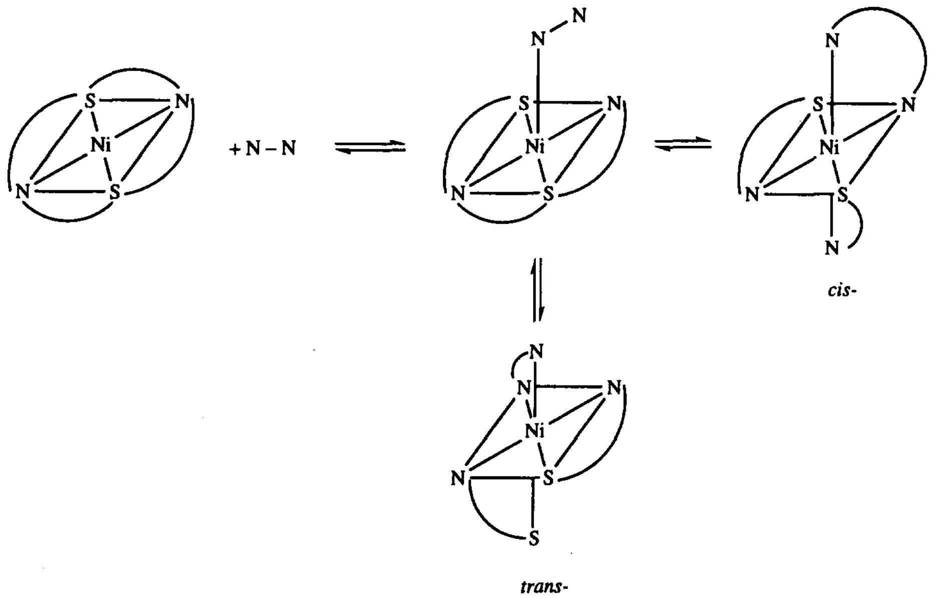


Fig. 2. Molecular structure and atom numbering of the cadmium complex (CdL$_2$I$_2$). The thermal ellipsoids are drawn at the 30% probability level. symmetry code: (a) $-x$ $1-y$, $-z$.



Scheme 1.

Table 4. Equilibrium constants for adduct formation at 25°C

Bidentate amine	Equilibrium constant K (dm^3 mol^{-1})	$\Delta A\infty$ (452 nm)
phen	1.10×10^5	0.68
5-NO$_2$phen	7.6×10^4	0.65
bipy	4.5×10^4	0.50
Me$_2$bipy	1.05×10^5	0.57
diafo		0

purified adduct of diafo and the adducts of phen are quite stable and easy to crystallize.

Although, in general, the mechanism of the addition process cannot be deduced from the structure data of the adducts [20–25], however, it is very interesting to discuss the possible mechanism of the addition process by the bidentate diamines to the square-planar nickel(II) complex. In general, there are two types of configuration of the possible adduct, as shown in Scheme 1.

The bidentate amine molecule approaches the planar nickel chelate in an axial direction. Suppose one Ni—N bond of the parent complex disrupts the chelate ring (the Ni—N bond was disrupted), so as to allow the two coordinated nitrogen atoms N(3) and N(6) of the two schiff base ligands in the *cis*-position. If one Ni—S bond of the parent complex was disrupted, the product would have been the *trans*-configuration of the two coordinated nitrogens N(3) and N(6) of the Schiff base ligands. The *cis*-configuration of N(3) and N(6) supported the former speculation, one Ni—N bond disrupts.

Acknowledgements—The work was supported by the National Nature Science Foundation and the Key Project from the National Science and Technique Commission of China.

REFERENCES

1. Coucouvanis, D., *Prog. Inorg. Chem.*, 1977, **26,** 301.
2. Gable R., Hoskins, B. and Winter, G., *Inorg. Chim. Acta*, 1973, **96,** 151.
3. Wasson, J. R., Woltermann, G. M. and Stoklosa, H. H., *Top. Curr. Chem.*, 1973, **35,** 65.
4. Cusumane, M., *Inorg. Chem.*, 1979, **18,** 3612.
5. Fayyaz, U. and Grant, M. W., *Aust. J. Chem.*, 1977, **30,** 285.
6. Grant, M. W. and Magee, R. J., *Aust. J. Chem.*, 1976, **29,** 749.
7. (a) Ali, M. A. and Livingstone, S. E., *Coord. Chem. Rev.*, 1974, **13,** 101; (b) Rahaman, M., Mridha, M. A. and Ali, M., *Trans. Met. Chem.*, 1994, **19,** 237.
8. Fun, H. K., Sivakumar, K., Yip, B. C., Tian, Y. P., Duan, C. Y., Lu, Z. L. and You, Y. Z., *Acta Cryst.*, 1995, **C51,** 2080.
9. Tian, Y. P., Duan, C. Y., Lu, Z. L., You, Y. Z. and Huang, X. Y., *J. Coord. Chem.*, 1996, **38,** 219.
10. (a) Tian, Y. P., Duan, C. Y., Lu, Z. L., You, X. Z., Fun, H. K. and Sivakumar, K., *Trans. Met. Chem.*, 1996, **21,** 254. (b) Tian, Y. P., Duan, C. Y., Lu, Z. L., You, X. Z., Fun, H. K. and Sivakumar, K., *Polyhedron*, 1994, **15,** 4425.
11. Tian, Y. P., Duan, C. Y., Lu, Z. L., You, X. Z., Fun, H. K. and Sivakumar, K., *Polyhedron*, 1996, **15,** 2263.

12. Newkome, G. R. and Roper, J. M., *J. Org. Chem.*, 1979, **44,** 502.
13. Tanner, J. and Krause, K. L., *The Rigaku J.*, 1994, **11,** 4. 1990, **7,** 38.
14. Kraus, K. L. and Phillips, G. N., *J. Appl. Cryst.*, 1992, **25,** 146.
15. Sheldrick, G. M., in *Computational Crystallography*, ed. D. Sayre. Oxford University Press, New York, 1982, pp. 506–514.
16. *International Tables for X-ray Crystallography*, ed, J. Ibers and W. C. Hamilton. Kynoch Press, Birmingham (now distributed by Kluwer Academic Press, Dorfrecht), 1974, pp. 55, 94,149.
17. Nanjo, M. and Yamasaki, T. *J. Inorg. Nucl. Chem.*, 1970, **32,** 2411.
18. Paulig, L., *The Nature of the Chemical Bond*, 3rd edn. Cornell University Press, NY Ithaca, U.S.A., 1960.
19. Brown, I. D. and Alternatt, D., *Acta Cryst.*, 1985, **B41,** 244.
20. Emmenegger, E. P., *Inorg. Chem.*, 1989, **28,** 2210.
21. Pierpont, C. G. and Eisenberg, R., *Inorg. Chem.*, 1970, **9,** 2218.
22. Shetty, P. S. and Fernando, Q., *J. Am. Chem. Soc.*, 1970, **92,** 3964.
23. Khare, G. P. and Eisenberg, R., *Inorg. Chem.*, 1970, **9,** 2211.
24. Sachinidis, J., Mackay, M. F. and Grant M. W., *Aust. J. Chem.*, 1979, **31,** 331.
25. Gable, R. W., Hoskins, B. F. and Winter, G., *Inorg. Chim. Acta*, 1985, **96,** 151.