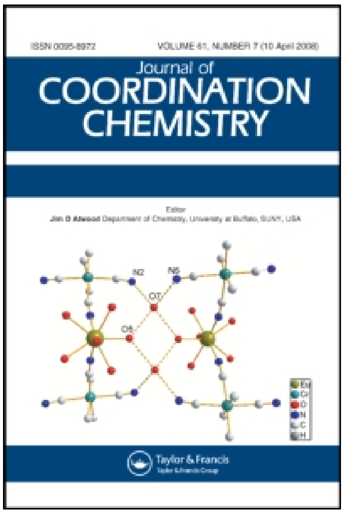

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Two new lead(II) nitrite complexes, crystal structure of $[Pb(phen)_2(NO_2)_2]$ an eight-coordinate lead(II) complex

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Two new lead(II) nitrite complexes, crystal structure of $[Pb(phen)_2(NO_2)_2]$ an eight-coordinate lead(II) complex

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Two new lead(II) complexes containing nitrite, $[Pb(L)_2(NO_2)_2]$, L = 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy), have been synthesized and characterized. The crystal structure of $[Pb(phen)_2(NO_2)_2]$ shows monomeric units. The coordination number is eight (four from "phen" ligands and four nitrite anions), weak interaction of lead(II) with oxygen atoms of adjacent molecules produce dimer units in the solid state. The arrangement of ligands exhibits a coordination hole around the lead(II), occupied possibly by a stereoactive lone pair of electrons on lead(II), and the coordination around lead is hemidirected. There is a π–π stacking interaction between the parallel aromatic rings that may help to increase the "gap" around lead(II).

Keywords: Lead(II) complexes; Nitrite ligand; Crystal structure; 1,10-phenanthroline; 2,2′-bipyridine

1. Introduction

Building new complexes and modifying their architectures in order to study their physical properties, has been a topic for many research groups. Many well-characterized bidentate ligands, such as "phen" or "bpy", complexes of lead(II) contain nitrate, perchlorate or thiocyanate anions and multifunction coordination mode anions such as nitrite ion have been described rarely [1–8]. The nitrite anion is an ambidentate ligand and can coordinate metal ions via both the N and O atoms. This anion is monodentate through oxygen to give a nitrito complex, or through nitrogen to give a nitro complex or bidentate through chelation, or by forming a bridge [9–13]. For these reasons, there are a variety of complexes containing nitrite. Here the synthesis and characterization of two new 1 : 2 adducts of 1,10-phenanthroline and 2,2′-bipyridine and lead(II) with nitrite counter ion are reported.

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2. Experimental

2.1. *Physical measurements*

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510 P spectrophotometers. Microanalyses were carried out using a Heraeus CHN–O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The ^{207}Pb solution NMR spectra were recorded on a Bruker DRX-500 AVANCE spectrometer at 104.6 MHz using a 5-mm broadband probe. Lead chemical shifts are reported (ppm) downfield from tetrametyllead using $Pbph_4$ ($\delta_{Pb} = -178.0$ ppm, saturated in $CDCl_3$) as an external standard. Each lead spectrum was acquired in 3–10 h.

2.2. *Preparation of [Pb(phen)$_2$(NO$_2$)$_2$] (1)*

The 1,10-phenanthroline (0.2 g, 1 mmol) was placed in one arm of a branched tube and mixtures of lead(II) acetate (0.36 g, 1 mmol) and sodium nitrite (0.138 g, 2 mmol) in the other. Methanol was carefully added to fill both arms, then the tube was sealed and the ligand-containing arm immersed in a bath at 60°C, while the other was at ambient temperature. After 10 days, yellow crystals (m.p. 233°C) were deposited in the cooler arm which were filtered off, washed with acetone and ether and air dried (0.356 g, yield 53%), m.p. 213°C. Found: C, 43.61; H, 2.38; N, 12.43; $C_{24}H_{16}N_6O_4Pb$. Calcd: C, 43.65; H, 2.42; N, 12.73%.

IR (cm^{-1}) selected bands: 740(s), 1010(s), 1212(vs), 1410(vs), 1590(s), 1618(s), and 3040(w).

^{1}H NMR (500.13 MHz; DMSO; ppm; δ): 8.10–8.30 (m, 4H), 8.55–9.00 (m, 2H), and 9.20–9.45 (m, 2H).

^{13}C-{^{1}H} NMR (125.7 MHz; DMSO; ppm; δ): 124.30, 127.50, 129.40, 139.30, 144.50, and 149.32.

UV-Vis: λ_{max} (nm) (H_2O, log $\lambda/M^{-1}\,cm^{-1}$) 430 (4.58).

^{207}Pb NMR (DMSO; ppm; δ) −2145.7.

2.3. *Preparation of Pb(bpy)$_2$(NO$_2$)$_2$ (2)*

This complex was prepared via an analogous method to that used for [Pb(phen)$_2$(NO$_2$)$_2$]. Reactant materials: bpy, lead(II) acetate, sodium nitrite, (2 : 1 : 2), yellow crystals, m.p. 205°C. Yield 306 g, 50%. Found: C, 39.80; H, 2.90; N, 13.20; $C_{20}H_{16}N_6O_4Pb$. Calcd: C, 39.21; H, 2.61; N, 13.72%.

IR (cm^{-1}) selected bands: 742(s), 1015(s), 1210(vs), 1410(vs), 1592(s), 1617(s), and 3030(w).

^{1}H NMR (500.13 MHz, DMSO; ppm; δ): 7.80 (t, 2H), 8.25 (q, 2H), 8.75 (d, 2H), and 7.80 (d, 2H).

^{13}C-{^{1}H} NMR (125.7 MHz, DMSO; ppm; δ): 127.50, 129.40, 139.30, 144.50, and 149.32.

UV-Vis: λ_{max} (nm) (H_2O, log $\lambda/M^{-1}\,cm^{-1}$) 420 (4.80).

^{207}Pb NMR (DMSO; ppm; δ) −2021.5.

Table 1. Crystal data and structure refinement for [Pb(phen)$_2$(NO$_2$)$_2$].

Identification code	[Pb(phen)$_2$(NO$_2$)$_2$]
Empirical formula	$C_{24}H_{16}N_{6}0_{4}Pb$
Formula weight	659.62
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 10.871(2)$ Å
	$b = 14.427(3)$ Å
	$c = 14.239(3)$ Å
	$\beta = 92.33(3)^\circ$
Volume	2231.4(8) Å^3
Z	4
Density (calculated)	1.963 Mg m^{-3}
Absorption coefficient	7.607 mm^{-1}
F(000)	1264
Crystal size	0.40 × 0.20 × 0.20 mm^3
Theta range for data collection	2.31–28.06°
Index ranges	$0 \le h \le 14$
	$0 \le k \le 19$
	$-18 \le l \le 18$
Reflections collected	7125
Independent reflections	5377 [R(int) = 0.0422]
Completeness to theta	99.4%
Absorption correction	Semi-empirical
Max. and min. transmission	0.3115 and 0.1508
Refinement method	Full-matrix least-squares on F^2
Data/Restraints/Parameters	5377/0/316
Goodness-of-fit on F^2	0.940
Final R [$I > 2\sigma(I)$]	indices for 4364 refl
R indices (all data)	$R_1 = 0.0341$, $wR_2 = 0.0852$
	$R_1 = 0.0410$, $wR_2 = 0.0874$
Largest diff. peak, hole	1.730, −0.963 e Å^{-3}

2.4. *Determination of the structure*

Crystallographic measurements were made at 293(2) K using a Siemens R3m/V diffractometer. The intensity data were collected within the range $2.31^\circ \le \theta \le 28.06^\circ$ using graphite monochromataed Mo–Kα radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. Intensities of 5377 unique reflections were measured, from which 4364 with $I > 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2.

The positions of hydrogen atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotropic thermal parameter. R_1, wR_2, with goodness-of-fit on F^2 (0.940) are 0.0341, 0.08520, respectively. The final difference density map showed a maximum peak and hole of 1.730 and −0.963 e Å^{-3}. Corrections for Lorentz and polarization effects as well as the empirical correction for absorption using semi-empirical programs were applied. All structural calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package [14, 15].

Crystal data and structure refinement are given in table 1. Selected bond lengths and angles are given in table 2. Anisotropic thermal parameters, observed and calculated

Table 2. Selected bond lengths (Å) and angles (°) for the [Pb(phen)$_2$(NO$_2$)$_2$].

Pb(1)–N(2)	2.497(4)
Pb(1)–O(2)	2.526(4)
Pb(1)–O(3)	2.550(4)
Pb(1)–O(1)	2.735(5)
Pb(1)–O(4)	2.833(4)
Pb(1)–N(3)	3.010(5)
Pb(1)–N(4)	3.038(5)
Pb(1)–N(1)	2.567(4)
N(2)–Pb(1)–O(2)	75.67(16)
N(2)–Pb(1)–O(3)	76.52(13)
O(2)–Pb(1)–O(3)	70.20(15)
N(2)–Pb(1)–N(1)	65.36(13)
O(2)–Pb(1)–N(1)	73.80(15)
O(3)–Pb(1)–N(1)	132.60(14)
N(2)–Pb(1)–O(1)	117.78(15)
O(2)–Pb(1)–O(1)	45.88(16)
N(2)–Pb(1)–O(4)	121.80(12)
O(2)–Pb(1)–O(4)	82.33(15)
O(3)–Pb(1)–O(4)	45.30(12)
N(1)–Pb(1)–O(4)	75.86(15)
N(2)–Pb(1)–N(3)	77.80(13)
O(2)–Pb(1)–N(3)	138.03(14)
O(3)–Pb(1)–N(3)	72.38(13)
N(1)–Pb(1)–N(3)	122.20(14)
O(1)–Pb(1)–N(3)	159.63(15)
N(2)–Pb(1)–N(3)	84.75(13)
N(2)–Pb(1)–N(4)	77.89(13)
O(2)–Pb(1)–N(4)	145.25(15)
O(3)–Pb(1)–N(4)	124.31(13)
N(1)–Pb(1)–N(4)	74.89(14)
O(1)–Pb(1)–N(4)	138.18(15)
O(4)–Pb(1)–N(4)	131.34(13)
N(1)–Pb(1)–N(4)	54.22(13)
O(3)–Pb(1)–O(1)	97.49(15)
N(1)–Pb(1)–O(1)	77.79(15)

structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. ORTEP diagrams and a perspective view of the packing in the unit cell are shown in figures 1 and 2.

3. Discussion

3.1. *Synthesis*

In the reaction of lead(II) salts with 1,10-phenanthroline or 2,2′-bipyridine ligands and nitrite anion, the products are normally obtained as powdered materials through conventional synthetic methods [16] and are typically insoluble in all organic solvents, so their structures are difficult to characterize. By diffusion along a thermal gradient in methanol solution (the branched tube method) lead(II) complexes in the crystalline form have been obtained. These compounds are yellow, air-stable and high-melting solids that are soluble in dimethylsulfoxide (DMSO). In the IR spectra of the nitrite lead(II) complexes the absorptions due to ν_{as} and ν_{sym} fall in the range 1410 and 1210–1212 cm^{-1}, respectively. The Δ value (ν_{as}–ν_{sym}) indicates that the nitrite anions coordinate to the lead(II) center as O,O-chelates [17].

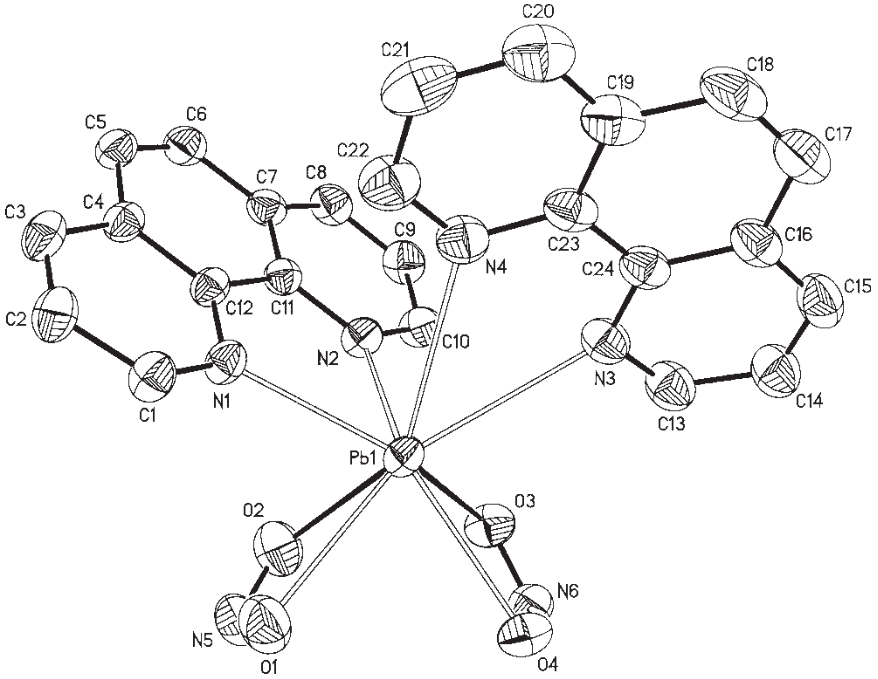

Figure 1. The ORTEP diagram of the [Pb(phen)$_2$(NO$_2$)$_2$].

3.2. *Crystal structure of [Pb(phen)$_2$(NO$_2$)$_2$] (1)*

The crystal structure of [Pb(phen)$_2$(NO$_2$)$_2$] consists of monomeric units with each lead chelated by the nitrogens of 1,10-phenanthroline ligands with Pb–N distances of 2.497, 3.010, 3.038 and 2.567 Å, and also the oxygens of nitrite unions with Pb–O distances of 2.526, 2.550, 2.735 and 2.833 Å (table 2). The coordination number in this complex is eight (four from "phen" ligands and four from nitrite anions). The weak interaction of lead(II) with oxygen atoms of adjacent molecules produce dimer units in the solid state. In fact, each Pb atom in this structure along with eight normal bonds forms one "weak" Pb$\cdots$O bond with distances of 3.150 Å. The presence of a lone pair of the lead atom is apparently the reason that the bridging interactions cannot be shorter. If the stereochemically active lone pair was not present, more bridging interactions between lead(II) and nitro ligands of the neighboring oxygen atoms might be possible, leading to more symmetry.

Determination of the structure of this material by X-ray crystallography (table 1) showed that the monomeric structure of this complex contains various similarities to the monomeric structures of [Pb(phen)$_2$(O$_2$ClO$_2$)$_2$] [1], [Pb(phen)$_2$(NO$_3$)$_2$] [1] and the dimer structure of [Pb(phen)$_2$(SCN)$_2$]$_2$ [18].

The arrangement of 1,10-phenanthroline and nitrite anions suggest a gap or hole in coordination geometry around the metal ion [O(2)–Pb–N(4) angle is 145.25° and O(1)–Pb–N(4) angle is 138.18°], occupied by a stereoactive lone pair of electrons on lead(II). A larger difference in the Pb–N distances of two 1,10-phenanthroline ligands exists with the Pb–N distances of 1,10-phenanthroline ligand *trans* to the lone pair at 2.497 and 2.567 Å, whereas, the Pb–N distances of 1,10-phenanthroline ligand

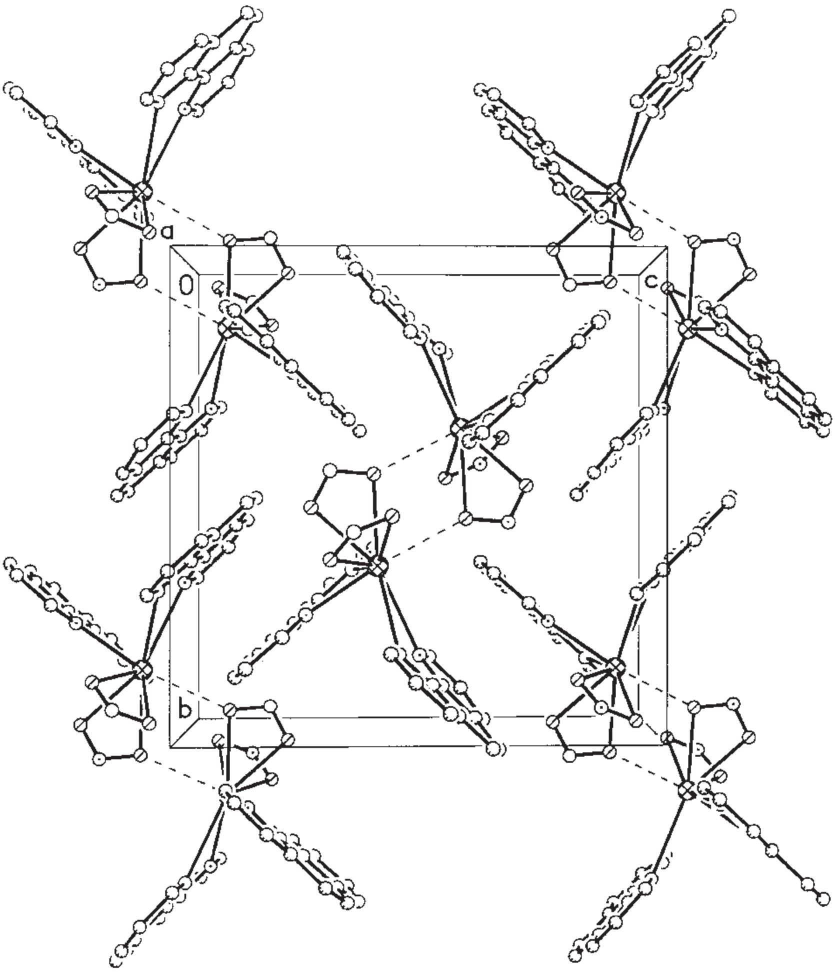

Figure 2. The unit cell of $[Pb(phen)_2(NO_2)_2]$.

cis to the lone pair are 3.010 and 3.038 Å, 0.5 Å difference. Shown in figure 3 are the two Pb–L distances (Pb–L_1 and Pb–L_2) for the hemidirected lead(II) compounds.

The increase in lone pair activity and increased interaction of the lone pair-Pb–L_1 may cause the difference between Pb–L_1 and Pb–L_2 angles to be larger.

The observed shortening of the Pb–N bonds on the side of Pb(II) ion opposite to the putative lone pair (2.497 and 2.567 Å compared with 3.010 and 3.038 Å adjacent to the lone pair) supports the presence of this feature [19]. Hence, the geometry of the nearest coordination environment of every lead atom is likely caused by the geometrical constraints of coordinated 1,10-phenanthroline ligands and nitrite anions and by the influence of a stereochemically active lone pair of electrons in a hybrid orbital on the metal. Such an environment leaves space for bonding of an oxygen atom of nitrite anion of an adjacent molecule (figure 2).

The possible stereochemical activity of the lone pair in divalent lead compounds has recently been discussed by Shimoni-Livny *et al.* based on a thorough review

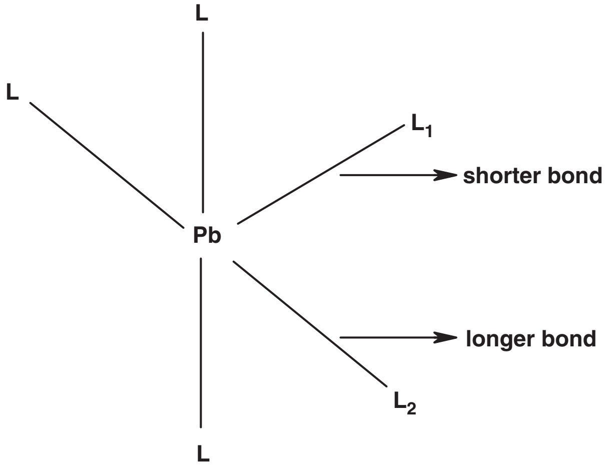

Figure 3. The Pb–L distances (Pb–L$_1$ and Pb–L$_2$) for the hemidirected lead(II) compounds.

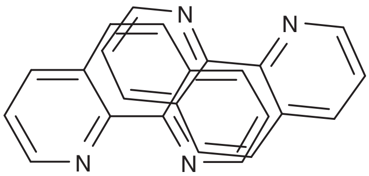

Figure 4. Projection of nearest neighbor pairs in the π–π stacks of the heteroaromatic bases in [Pb(phen)$_n$(NO$_2$)$_2$].

of crystal data available at the Cambridge Structural Database (CSD) [20]. They classify lead coordination as holodirected, which refers to complexes in which the bonds to ligand atoms are directed throughout the surface of an encompassing sphere, while hemidirected refers to those cases in which the bonds to ligand atoms are directed through only part of the coordination sphere, leaving a gap in the distribution of bonds to the ligand. For the structure described here, coordination around the lead atoms is hemidirected with a significant gap *trans* to the one 1,10-phenanthroline ligand.

The striking similarity between [Pb(phen)$_2$(NO$_3$)$_2$] [1], [Pb(phen)$_2$(ClO$_4$)$_2$] [1] and [Pb(phen)$_2$(NCS)$_2$]$_2$ [18] with the complex described here are π–π stacking [21, 22] interactions between the parallel aromatic rings belonging to adjacent chains in all three compounds, as shown in figures 2 and 4. In the structure reported here, the interplanar distance is 3.62 Å.

A simple model to describe π–π interactions has been developed by Hunter *et al.* [23]. This model predicts that face-to-face π-stacked interactions will be disfavored due to the dominance of π–π repulsion [24, 25]. Hence, within the molecule discussed here the electron-poor pyridyl rings interact with less electron-poor rings such as phenyl groups (figure 4).

Thus two factors, lone pair activity and π–π stacking, control the coordination sphere of these complexes. Whether the π–π stacking between the parallel aromatic rings helps to increase the "gap" in the coordination sphere around the metal ion or whether the “hole” from the “stereochemical activity” of valence shell lone electron pairs helps to form π–π stacking is not clear. However, self-assembly of these complexes is likely caused by both lone pair activity and the π–π stacking interactions.

Supplementary material

Crystallographic data for the structures reported in the article have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary material, CCDC No. 183432, for [Pb(phen)$_2$(NO$_2$)$_2$]. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. e-mail: deposit@ccdc.cam.ac.uk.

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References

[1] (a) J.M. Harrowfield, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White. *Aust. J. Chem.*, **49**, 1029 (1996); (b) J.M. Harrowfield, H. Miyamae, T.M. Shand, B.W. Skelton, A.A. Soudi, A.H. White. *Aust. J. Chem.*, **49**, 1043 (1996); (c) J.M. Harrowfield, H. Miyamae, T.M. Shand, B.W. Skelton, A.A. Soudi, A.H. White. *Aust. J. Chem.*, **49**, 1051 (1996); (d) J.M. Harrowfield, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White. *Aust. J. Chem.*, **49**, 1067 (1996); (e) J.M. Harrowfield, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White. *Aust. J. Chem.*, **49**, 1081 (1996); (f) G.A. Bowmaker, J.M. Harrowfield, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White. *Aust. J. Chem.*, **49**, 1089 (1996); (g) I. Bytheway, L.M. Engelhardt, J.M. Harrowfield, D.L. Kepert, H. Miyamae, J.M. Patrick, B.W. Skelton, A.A. Soudi, A.H. White. *Aust. J. Chem.*, **49**, 1099 (1996); (h) L.M. Engelhardt, J.M. Harrowfield, D.L. Kepert, H. Miyamae, J.M. Patrick, B.W. Skelton, A.A. Soudi, A.H. White. *Aust. J. Chem.*, **49**, 11112a (1996); (I) J.M. Harrowfield, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White. *Aust. J. Chem.*, **49**, 1121 (1996); (j) J.M. Harrowfield, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White. *Aust. J. Chem.*, **49**, 1127 (1996); (k) L.M. Engelhardt, J.M. Harrowfield, D.L. Kepert, H. Miyamae, J.M. Patrick, B.W. Skelton, A.A. Soudi, A.H. White. *Aust. J. Chem.*, **49**, 1135 (1996); (l) J.M. Harrowfield, D.L. Kepert, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White. *Aust. J. Chem.*, **49**, 1147 (1996); (m) J.M. Harrowfield, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White. *Aust. J. Chem.*, **49**, 1157 (1996); (n) J.M. Harrowfield, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White. *Aust. J. Chem.*, **49**, 1165 (1996).
[2] J. Parr. *Polyhedron*, **16**, 551 (1997).
[3] A.K. Hall, J.M. Harrowfield, A. Morsali, A.A. Soudi, A. Yanovsky. *Cryst. Eng. Comm.*, **13**, 282, (2000).
[4] A. Morsali, M. Payheghader, M.S. Salehi. *Z. Anorg. Allg. Chem.*, **628**, 12 (2002).
[5] A.R. Mahjoub, A. Morsali. *Polyhedron*, **21**, 197 (2002).
[6] A. Morsali, A.R. Mahjoub, S. Janitabar Darzi, M.J. Soltanian. *Z. Anorg. Allg. Chem.*, **629**, 2599 (2003).
[7] A. Morsali, X.-M. Chen. *J. Coord. Chem.* **57**, 1233 (2004).
[8] A. Morsali, M. Payheghader, M.S. Salehi, M. Moradi. *J. Coord. Chem.*, **56**, 761 (2003).
[9] I. Resino, M. Monfort, J. Ribas, M.F. Bardia, X. Solans. *Polyhedron*, **19**, 225 (2000).
[10] A. Gleizes, A. Mayer, M.A. Hotchman, O. Kahn. *Inorg. Chem.*, **21**, 2257 (1983).
[11] A.J. Finney, M.A. Hotchman, C.L. Raston, G.L. Rowbottom, A.H. White. *Aust. J. Chem.*, **34**, 2139 (1981).
[12] D.M.L. Goodgame, M.A. Hitchman, D.F. Marsham, P. Phavanantha, D. Rogers. *J. Chem. Soc., Dalton Trans.*, 1383 (1969).
[13] L.K. Chou, K.A. Abboud, D.R. Talham, W.W. Kim, M.W. Meisel. *Chem. Mater.*, **6**, 2051 (1994).
[14] G. Ferguson, C. Glidewell, E.S. Lavender. *Acta Crystallogr.*, **B55**, 591 (1999).
[15] G.M. Sheldrick. *SHLXTL-97*, V5.10, Bruker AXS Inc., Madison, WI 53719, USA (1997).
[16] N. Masciocchi, P. Cairati, L. Carlucci, G. Ciani, A. Sironi. *J. Chem. Soc., Dalton Trans.*, 2739 (1996).
[17] M.A. Hitchman, G.L. Rowbottom. *Coord. Chem. Rev.*, **42**, 55 (1982).

[18] L.M. Engelhardt, J.M. Harrowfield, D.L. Kepert, J.M. Patrick, B.W. Skelton, A.H. White. *J. Chem. Soc., Dalton Trans.*, 595 (1989).
[19] R.D. Hancock, M.S. Shaikjee, S.M. Dobson, J.C.A. Boeyens. *Inorg. Chim. Acta*, **154**, 229 (1988).
[20] L. Shimoni-Livny, J.P. Glusker, C.W. Bock. *Inorg. Chem.*, **37**, 1853 (1998).
[21] N.N. Greenwood, A. Earnshaw. *Chemistry of the Elements*, pp. 235–236, Pergamon Press, Oxford (1986).
[22] R. Foster (Ed.). *Molecular Complexes*, Paul Elek (Scientific Books) Ltd, London (1973).
[23] C.A. Hunter, J.K.M. Sanders. *J. Am. Chem. Soc.*, **112**, 5525 (1990).
[24] J.M. Steed, T.A. Dixon, W. Klemperer. *J. Chem. Phys.*, **70**, 4940 (1979).
[25] J.C. Collings, K.P. Roscoe, E.G. Robins, A.S. Batsanov, L.M. Stimson, J.A.K. Howard, S.J. Clark, T.B. Marder. *New J. Chem.*, **26**, 1740 (2002).