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Stereochemical trends of metal derivatives of some heterocyclic-2-thiones and thiosemicarbazones

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Abstract. The interaction of heterocyclic thiones/thiosemicarbazones with metals has been the subject of several investigations as these ligands contain chemically active groups, –N(H)–C(=S)– ↔ –N=C(–SH)– ,and are useful model compounds for sulphur-containing analogues of purine and pyrimidine bases. Heterocylic-2-thiones bind to metals in several ways and lead to the formation of monomeric or polymeric complexes. For example, the simplest prototype of heterocylic-2-thiones, namely, pyridine-2-thione has several ways of binding, notably, terminal S-bonding and S-bridging (in neutral form), while in anionic form the modes are terminal S-bonding, S-bridging, N,S-chelation, N,S-bridging, N,S-chelation-cum-S-bridging and N,S-bridging-cum-S-bridging. Similarly, thiosemicarbazones bind to metals as S-bonded unidentates or N,S-chelates. In this paper, the chemistry of pyridine-2-thione, its N-oxide, 2-(benzylthio)pyridine-1-oxide thione with metals like iron(II), ruthenium(II), nickel(II), palladium(II), platinum(II), copper(I), copper(II), silver(I) and mercury(II) is briefly described. As regards thiosemicarbazones, focus is only on two compounds, namely organomercury(II) and organothallium(III). A variety of new molecules, well characterised by NMR and X-ray crystallography, is introduced.

Keywords. Heterocyclic thiones; thiosemicarbazones; tertiary phosphines; coordination properties; pyridine-2-thione; 1-hydroxy-pyridine-2-thione.

1. Introduction

The coordination chemistry of heterocyclic thiones containing –N(H)–C(=S)– ↔ –N=C(–SH)– functional group is of immense interest because such compounds (a) mimic cysteine sulphur coordination in metalloenzymes; (b) show electronic and structural properties of the active sites in copper blue proteins involving S,N-coordination and (c) comprise purine and pyrimidine bases. In addition, these and their N-oxide derivatives have been found to have considerable biochemical properties. Similarly, thiosemicarbazones containing the –N=NH–C(=S)– ↔ =N–N=C(–SH)– group are important ligands due to coordination with a variety of donor atoms and their numerous biochemical properties [1–10].

In this paper, the coordination properties of pyridine-2-thione (HpyS, C_5H_5NS), 1-hydroxy-pyridine-2-thione (HpyOS, C_5H_5NOS), 2-(benzylsulphanyl)-pyridine-1-oxide (pyOSBz) and a series of thiosemicarbazones with tertiary phosphines as co-ligands are described. The metals used for the synthesis of the compounds are Fe, Ru, Ni, Pd, Pt, Cu, Ag, Hg and Tl.

2. Heterocyclic thione derivatives of metals

This section discusses details of work done with heterocyclic thiones mentioned in the introduction.The strategy here is to provide the main features of the work with all the attendant information available from the references. For convenience, the work is split into different groups.

2.1 *Iron and ruthenium*

In the case of iron, though several reactions were carried out, not much could be established. Reaction of anhydrous $FeCl_3$ with HpyS in ethanol followed by the addition of a tertiary phosphine was carried out to prepare an octahedral complex $FeCl_2$(pyS-N,S)$(PPh_3)_2$. However, the product turned out to be $FeCl_2(HpyS)_2$ (**1**) whose X-ray study established tetrahedral structure with HpyS binding to Fe(II) via S donor atom and the free NH group forming an intermolecular hydrogen bond with Cl atoms of adjacent molecules [11]. There was the expected oxidation of HpyS to pySSpy, but the same was not established. Later on, another group [12] carried out the reaction of $FeCl_3$ with HpyS in ethanol at room temperature and isolated the product $[pySSpyH]^+[FeCl_4]^-$. Due to the complex behaviour of iron in these systems, our efforts to synthesize several mixed ligand complexes of the type FeX_2(pyS-N, S) (diphosphine) (X = Cl, Br, I), with HpyOS ditertiary phosphine were not successful.

In contrast, ruthenium(II) showed the expected behaviour. The reaction of $Ru(PPh_3)_3Cl_2$ with HpyS (1:2 ratio) in benzene or toluene in presence of triethylamine formed Ru(pyS-N,S)$_2(PPh_3)_2$ (**2**), which has a distorted (*cis*, *cis*, *trans* : : N,N; P,P; S,S) octahedral structure [13]. Similar reaction of $Ru(dppe)_2Cl_2$ {dppe = $Ph_2P–(CH_2)_2–PPh_2$} with HpyS in presence of Et_3N in benzene did not form Ru(pyS–N,S)$_2$(dppe) (**3**), instead crystals of $Ru(dppe)_2Cl_2$ were formed having *trans*-octahedral structure with chelating dppe [14]. **3** was then prepared by replacing PPh_3 from **2** by dppe in benzene as solvent [15]. Reaction of **2** with a tritertiary phosphine $\{Ph_2P–CH_2–CH_2\}_2P(Ph)$ (triphos) also formed Ru(pyS–N,S)$_2$ (triphos–P,P) (**4**) with one pendant Ph_2P-group. The compounds with dppm, dppp and dppb {$Ph_2P–(CH_2)_m–PPh_2$, *m* = 1, dppm, *m* = 3, dppp and *m* = 4, dppb}, as well as derivatives of HpyOS were prepared by the method used for **2** [15]. The X-ray structures of Ru(pyS)$_2$(L–L) {L–L = dppe, **3** [16], dppp, **5** [17] and dppb, **6** [18], also showed structures similar to that of **2**. The *trans*-S–Ru–S bond angles are similar, 154·7–155·9°; however, *cis*-P–Ru–P and *cis*-N–Ru–N bond angles vary in the order, N–Ru–N, *m* = dppe > dppp > dppb and P–Ru–P and *m* = dppb > dppp > dppe. Thus shorter the chain length connecting Ph_2P-groups, larger the N–Ru–N bond angle {PRuP angles are in the range, 84·1–94·3°; NRuN angles in the range, 82·3–87·5°}. **2** showed largest PRuP and shortest NRuN angles {96·8°, 80·9° respectively}. High resolution ^{13}C NMR study of **5** showed that Ph groups on P are non-equivalent as two sets of triplets for *i, o, m* carbons were found [17]. The magnetic non-equivalence of Ph groups is due to the relative orientation of the pyridyl group to one of the Ph groups of the Ph_2P moiety. Further, complexes were found to undergo one-electron redox reactions as shown by cyclic voltammetric studies [15].

2.2 *Nickel, palladium and platinum*

2.2a *Nickel(II):* Only a few nickel compounds have been studied due to lack of interaction of Ni(pyOS)$_2$ {obtained from $NiCl_2.6H_2O$ and Na^+ $pyOS^-$} moiety with

tertiary phosphines – this being of interest to us in the study in mixed-ligand complexes containing heterocyclic thiones and tertiary phosphines [19]. Thus a few compounds with 2,2′-pyridyl (bipy) and 1,10-phenanthroline (phen) have been reported. Reaction of $Ni(pyOS)_2$ with bipy in chloroform formed two isomers, **7** (parrot-green) and **8** (yellow-brown). While the former is diamagnetic (major) the latter is paramagnetic (minor) [19]. The diamagnetic is believed to be having NiN_2S_2 atoms in the square planar geometry of **7** with the O atoms having weak or no interaction along the *z*-axis. $Ni(pyOS)_2$(phen) (**9**) was prepared by the same method and showed no isomers like bipy compounds. **8** and **9** showed intermediate magnetic moment values with m= 2·55 BM.

2.2b *Palladium(II) and platinum(II):* Palladium(II) acetate with HpyS forms N,S-bridged dimer $\{Pd_2(pyS–N,S)_4\}$ (**10**) [20] and the same can be prepared from $PdCl_2$ and Na^+pyS^- in CH_3CN solvent [21]. Reaction of **10** with PPh_3 in 1:2 mole ratio formed $Pd(pyS–S)_2(PPh_3)_2$ (**11**) having *trans*-square planar geometry[21] which was proposed on the basis of ^1H and ^{13}C NMR data and X-ray structure of an analogous Pt complex **12** (*vide infra*). Similarly, reaction of N,S-bridged dimer $Pt_2(pyS\text{-}N,S)_4$ {obtained from $PtCl_2$ and Na^+pyS^- in CH_3CN} with PPh_3 in 1:2 (Pt:PPh_3) mole ratio formed monomeric $Pt(pyS\text{-}S)_2(PPh_3)_2$ **12** having S-bonded pyridine-2-thionate groups in *trans* orientation as established by X-ray crystallography [22]. **12** was found to dissociate in $CHCl_3$ solution as shown by ^{31}P NMR spectroscopy,

$$\underset{\mathbf{12}}{Pt(pyS)_2(PPh_3)_2} \rightarrow \underset{\mathbf{12a}}{Pt(pyS)_2(PPh_3)} + PPh_3. \quad (1)$$

12a was shown to have both N,S-chelated and S-bonded pyS moieties by ^{13}C NMR spectroscopy [22]. Other tertiary phosphine derivatives structurally established are Pd(pyS–N,S)Cl(PPh_3) [23] and $[Pt(pyS–N,S)(PPh_3)_2]^+(PF_6)^-$ [24].

The use of diphosphines in place of PPh_3 also gave interesting results. From $PtCl_4$, HpyS and dppe or dppen in presence of Et_3N in the solvent benzene, the compounds, $[Pt(pyS\text{-}S)_2(L–L)]$ {L–L = dppe, **13**, dppen ($Ph_2PCH=CHPPh_2$), **14**} were formed containing chelating diphosphines and S-bonded pyS groups with pendant pyridyl groups [25] which are confirmed by ^{13}C NMR and X-ray crystallography. A similar product, $[Pd(pyS–S)_2(L–L)]$ {L–L = dppe, **15**} was formed from $[PdCl_2(dppe)]$ and HpyS in presence of sodium hydroxide [25]. All three have been established with X-ray crystallography and represent the first examples of Pt^{II}/Pd^{II} complexes containing *cis* pendant pyridyl groups which may act as precursors for polymeric complexes. The ^{31}P NMR spectra of **14** showed ^{31}P signals with a pair of satellites due to coupling from ^{195}Pt (I = 1/2) while **13** showed one ^{31}P signal with a pair of satellites. The presence of two sets of ^{31}P signals could be due to the non-equivalent pyridyl groups opposite the P atoms and this non-equivalence is probably not resolved in case of the dppe complex **13**. While the $J_{P–Pt}$ constants are similar in magnitude in the two cases [**13**, $J_{P–Pt}$, 2968·2 Hz, **14**, $J_{P–Pt}$, 2958·5, 2969·4 Hz), the coordination shifts are different [**13**, ΔdP 58·2, **14**, ΔdP 77·1 ppm]. Thus dppen was found to coordinate more strongly to the Pt centre than dppe. The difference is attributed to the unsaturation in the –CH=CH– moiety of dppen which could favour increased charge delocalisation in the Pt-dppen moiety. With other diphosphines and phosphine chalcogenides similar products have been prepared [25].

The HpyOS derivatives of Pd/Pt of the type $M(pyOS\text{-}O,S)_2$ showed poor tendency to form tertiary phosphine complexes and none could be established from X-ray

crystallography [21]. It is interesting to point out that whereas Pd(pyOS–O,S)$_2$ showed only one species having *cis*-sulphur atoms, NMR showed two isomers for Pt(pyOS)$_2$ having *cis*- and *trans*-isomers with respect to O,S-donor atoms [21].

2.3 *Copper*

Reaction of $CuCl_2.2H_2O$ with HpyS in ethanol forms an insoluble ESR inactive material of composition CuCl(HpyS) which on reaction with two equivalents of Ph_3P in $CHCl_3$ formed the product [CuCl(HpyS–S)(PPh_3)$_2$], **16**. Similarly, with ditertiary phosphines, the compounds, [CuCl(HpyS–S)(L–L)] {L–L = dppm, dppe, dppp and dppb} were formed and the behaviour of copper(II) bromide salt was identical [26,27]. X-ray crystallography of **16** established tetrahedral structure with NH.....Cl intramolecular hydrogen bonding [27]. It was interesting to know that there was no reaction with Ph_3PO, Ph_3PS, Ph_3PSe and Ph_3As and this supports the fact that tertiary phosphines are strong Lewis bases vis-a-vis phosphine chalcogenides or arsines, as mentioned above [26]. In the case of HpyOS, similar reactions formed Cu^{II} complexes, CuX(pyOS–O,S)(L_2) or CuX(pyOS–O,S)(L–L) {L = Ph_3P and L–L = diphosphines as mentioned above} which were ESR active (here HpyOS behaved as an anionic ligand). However, none could be crystallised to establish molecular structure [28]. Unlike Ph_3P or diphosphines, the substituted tertiary phosphines namely tri-*p*-tolyl (*p*-Tol_3P) and tri-meta-tolyl phosphines (*m*-Tol_3P) with copper(I) halides and HpyS formed 1:1:1 complexes of the type [CuX(HpyS–S)(PR_3)] (X = Cl, Br, I) which were established to be dimeric using X-ray crystallography [29]. The dimer formation occurs via S donor atoms. Weak Cu....Cu or S...S interactions were noticed in the central moiety Cu_2S_2 with R_3P and X groups in *trans*-position and the free-end NH of HpyS having NH...X intra-molecular hydrogen bonding. Interestingly for X = Br and R_3P = Ph_3P, both 1:1 and 1:2 products were established [30]. For the dimeric complexes, ^{31}P NMR showed dissociation as follows

$$[CuX(HpyS)L]_2 \leftrightarrow Cu_2X_2(HpyS)_2L + L, \quad (X = Cl, Br, I; L = m\text{-}Tol_3P, p\text{-}Tol_3P). \tag{2}$$

Like Ni(II), copper(II) formed only one adduct with phen in chloroform having stoichiometry, Cu(pyOS)$_2$(phen).3/4$CHCl_3$ (**17**) and conductance showed the product to have the formulate as, [Cu(pyOS)(phen)$_2$][Cu(pyOS)$_3$]1·5$CHCl_3$ [19]. **17** is ESR active and the spectrum is commensurate with an elongated structure.

2.4 *Silver and mercury*

Silver(I) complexes, Ag(pyOS)-O,S)(L) [L = dppm, **18**, dppb, PPh_3, and *m*-Tol_3P] were obtained from silver(I) acetate and neutral HpyOS in water–ethanol medium followed by addition of tertiary phosphines. Direct reaction of mercury(II) halides with 2-(benzylthio)pyridine-1-oxide (pyOSBz-O) in ethanol formed HgX_2(pyOSBz) [X = Cl, **19**, Br]. Similarly, organomercury(II) derivatives, RHgL [R = *m*-$NO_2C_6H_4$–, L = pyS^-, $pyOS^-$; R = *p*-ClC_6H_4–, L = pyS^-, $pyOS^-$; R = C_6H_5–, L = pyS^-, **20**, $pyOS^-$] were prepared from Hg(R)($OOCCH_3$) and neutral pyridine-2-thiones HpyS or HpyOS). **18** exists as a dimer with dppm bridging the two Ag atoms leading to the formation of an eight-membered metallacyclic ring with pyOS moieties chelating to each Ag atom via O,S-donor atoms. The geometry about each Ag centre is a highly distorted tetrahedral with

bond angles varying from 72·85(7)^{o} to 137·92(4)^{o}. Compounds **19** and **20** acquire formally dimeric structures via weaker interactions. For example in **19**, Hg binds strongly to one O atom and two Cl atoms, and weakly to one Cl atom and one S atom of the second molecule. The geometry about each Hg atom is formally highly distorted trigonal bipyramidal with Cl(1)–Hg–Cl(2) and O(1)–Hg-S(1)* bond angles of 172·84(5) and 151·70(9)^{o} respectively. Finally in **20**, Hg is bonded strongly to one C and one S atom, relatively weakly to N{Hg–N, 2·795(10), 2·879(9)Å} and very weakly to the second S atom of the second molecule {Hg-S, 3·312(3), 3·365(3)Å}. If secondary interactions are ignored, the geometry about the Hg atom is formally distorted T-shaped [31]. The tricoordinate complex {Ag(pyOS-O,S)(PPh_3)} is also dimeric with the Ag_2S_2 central moiety, terminal PPh_3 molecules and chelating $pyOS^-$ groups [32] dimerising via S-atoms.

3. Thiosemicarbazone derivatives of metals

3.1 *Mercury*

The reactions of phenylmercury(II) acetate with a series of thiosemicarbazones in ethanol medium at room temperature formed novel phenylmercury(II) thiosemicarbazonates of stoichiometry [HgPh(L)] {HL : R = N^3–N^2H–C^1(S)–N^1H_2, cyclopentanone (**21**), cyclohexanone (**22**), benzaldehyde **(23**), 4-methoxybenzaldehyde (**24**), pyrrole-2-carbaldehyde **(25**), thiophene-2-carbaldehyde (**26**) and furan-2-carbaldehyde (**27**) thiosemicarbazones} [33]. The ^{1}H and ^{13}C NMR data suggest that the thiosemicarbazones deprotonate the most acidic hydrazinic N^2H proton during reaction with phenylmercury(II) acetate and coordinate to Hg(II) via chelating N^3,S-donor atoms. ^{199}Hg NMR data suggest symmetrisation phenomenon as below for complexes **23** and **24**, which is supported by ^{1}H and ^{13}C NMR data.

$$2[HgPhL] \rightleftharpoons HgPh_2 + HgL_2. \quad (3)$$

Mercury chemical shift values reveal that shielding of Hg with the change of organic groups in the thiosemicarbazones decreases in the order: 2-hydroxybenzene >>> furan > benzene > 4-methoxybenzene >> thiophene ≈cyclohexanone ≈cyclopentanone > pyrrole while the Lewis acidity of the thiosemicarbazones varies in the reverse order. The ^{1}H and ^{13}C NMR data reveal that **26** and **27** show isomerism. The weak intermolecular interactions via Hg....N^2 in **21** and via Hg...S in **24** and **25** form centrosymmetric dimers and Hg formally acquires four coordination with two strong (Hg-C, Hg-S), one weak (Hg.....N^3) and one secondary (Hg.....N^2 or S) bonds. The preferred dimer formation via N^2 nitrogen in **21**, rather than via sulphur atoms (**24** and **25**) despite Hg....S affinity, represents an unusual bonding mode. The low temperature studies show that the energy barrier to rotation of N^1H group about C^1–N^1 bond varies in the order **24** > **25** ~ **21** > **22**.

It may be interesting to know that whereas acetophenone thiosemicarbazone (R = N^3-N^2H–C^1(S)–N^1H_2, R = acetophenone) reaction with PhHg(OAc) forms black material, the same reaction with PhHgCl leads to symmetrisation phenomenon as noted in some complexes mentioned above [34]:

$$2PhHgCl + L \rightarrow Ph_2Hg + HgCl_2L_2. \quad (4)$$

3.2 *Thallium(III)*

The reactions of diphenylthallium(III) hydroxide with a series of thiosemicarbazones in water–ethanol medium at room temperature formed novel diphenylthallium(III) thiosemicarbazonates of stoichiometry $[TlPh_2(L)]$ {HL : R = N^3–N^2H–C^1(S)–N^1H_2, cyclopentanone (**28**), benzaldehyde (**29**), 2-hydoxybenzaldehyde (**30**), 4-methoxybenzaldehyde (**31**), acetophenone (**32**), furan-2-carbaldehyde (**33**), pyridine-2-formaldehyde (**34**), and pyridine-2-acetaldehyde thiosemicarbazones (**35**)} [35]. ^{1}H and ^{13}C NMR data suggest that the thiosemicarbazones deprotonate the most acidic hydrazinic N^2H proton during reaction with $TlPh_2(OH)$ and coordinate to Tl(III) via chelating N^3,S-donor atoms (**28–33)** or chelating N^4,N^3,S-donor atoms (**34** and **35)**. In all the cases, thiosemicarbazones change the conformation from E-mode to Z-mode. ^{205}Tl NMR suggest more than one species involving intra- or inter-molecular interactions for **28–33** and only one species for **34** and **35**. Thallium chemical shift values reveal that the shielding of Tl with the change of organic group in the thiosemicarbazones decreases in the order, 2-formyl-pyridine > 2-acetyl-pyridine > 2-hydroxybenzene > benzene > 4-methoxy-benzene > furan > 2-acetyl-benzene > cyclopentanone. In **28**, Tl(III) is bonded to two carbon atoms of phenyl group [Tl-C, 2·146(6), 2·148(6)Å], N^3 and S atoms [Tl-N^3, 2·55(1)Å; Tl-S, 2·616(3)Å] of deprotonated cyclopentanone thiosemicarbazones (Hcptsc). The C^7–Tl–C^{13} and N^3–Tl–S bond angles of 146·6(2) and 72·90(12)^o suggest a distorted trigonal bipyramid geometry with one vacant site in the equatorial plane. **34** and **35** exist as 3-independent molecules each with distorted trigonal bipyramid geometry. Tl is coordinated to two carbon atoms and N^3, N^4 and S atoms of deprotonated pytsc and acpytsc anions. The bond lengths and angles of 3-independent molecules of both **34** and **35** are different though similar to those for **28**. The existence of 3-independent molecules in the lattice represents novel and unusual examples in organothallium(III) chemistry. The low temperature proton NMR studies of **34** and **35** reveal that the energy barrier to rotation of the amino groups about C^1–N^1 bond is a bit higher than that in analogous PhHg(II) systems.

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References

1. Raper E S 1985 *Coord. Chem. Rev.* **61** 115
2. Raper E S 1996 *Coord. Chem. Rev*. **153** 199
3. Campbell M J M 1975 *Coord. Chem. Rev*. **15** 279
4. Padhye S B and Kauffman G B 1985 *Coord. Chem. Rev*. **63** 127
5. West D X, Padhye S B and Sonawane P B 1991 *Struct. Bonding (Berlin*) **76** 4
6. West D X, Liberta A E, Padhye S B, Chilate R C, Sonawane P B, Kumbhar A S and Yerande R G 1993 *Coord. Chem. Rev*. **123** 49
7. Lobana T S and Bhatia P K 1989 *J. Sci. Ind. Res.* **48** 394
8. Rodriguez-Arguelles M C, Ferrari M B, Fava G G, Pelizzi G, Tarasconi P, Albertini R, Dall'Aglio P P, Lunghi P and Pinelli S 1995 *J. Inorg. Biochem.* **58** 157
9. Casas J S, Garcia-Tasende M S, Maichle-Mossmer C, Rodriguez-Arguelles M C, Sanchez A, Sordo J, Vazquez-Lopez A, Pinelli S, Lunghi P and Albertini R 1996 *J. Inorg. Biochem*. **62** 41

10. Ferrari M B, Fava G G, Tarasconi G, Albertini R, Pinelli S and Starcich R 1994 *J. Inorg. Biochem.* **53** 13
11. Povey D C, Smith G W, Lobana T S and Bhatia P K 1991 *J. Crystallogr. Spectrosc. Res.* **21** 9
12. Couce M D, Russo U and Valle G 1995 *Inorg. Chim. Acta* **234** 195
13. Fletcher S R and Skapski A C 1972 *J. Chem. Soc., Dalton Trans.* 635
14. Lobana T S, Singh R and Tiekink E R T 1990 *J. Coord. Chem.* **21** 225
15. Lobana T S and Singh R 1995 *Polyhedron* **14** 907
16. Tiekink E R T, Lobana T S and Singh R 1991 *J. Crystallogr. Spectrosc. Res.* **21** 205
17. Lobana T S, Verma R, Singh R and Castineiras A 1998 *Transition Met. Chem*. **23** 25
18. Horn E, Lobana T S, Singh R and Tiekink E R T 1993 *Z. Kristallogr*. **205** 291
19. Lobana T S and Paul S 1996 *Transition Met. Chem.* **21** 300
20. Rosenfield S G, Berends H P, Gelmini L, Stephen D W and Masacharak P K 1987 *Inorg. Chem*. **26** 2792
21. Lobana T S and Verma R 1999 *Indian J. Chem. Sect. A* **38** 592
22. Lobana T S, Verma R and Castineiras A 1998 *Polyhedron* **17** 3753
23. Nakatsu Y, Nakamura Y, Matsumoto K and Ooi S 1992 *Inorg. Chim. Acta* **196** 81
24. Wang S, Staples R J and Fackler J P Jr 1994 *Acta Crystallogr.* **C50** 889
25. Lobana T S, Verma R, Hundal G and Castineiras A 1999 *Polyhedron* (in press)
26. Lobana T S and Bhatia P K 1990 *Indian J. Chem.* **A29** 1225
27. Lobana T S, Bhatia P K and Tiekink E R T 1989 *J. Chem. Soc., Dalton Trans*. 749
28. Lobana T S and Bhatia P K 1992 *J. Chem. Soc., Dalton Trans*. 1407
29. Lobana T S, Paul S and Castineiras A 1997 *Polyhedron* **16** 4023
30. Karagiannidis P, Aslandis P, Kessissoglou D P, Krebs D and Dartmann M 1989 *Inorg. Chim. Acta* **156** 47
31. Lobana T S, Paul S and Castineiras A 1999 *J. Chem. Soc., Dalton Trans.* 1819
32. Lobana T S, Paul S, Hundal G and Obrai S 1999 *Transition Met. Chem*. **24** 202
33. Lobana T S, Sanchez A, Casas J S, Castineiras A, Sordo J, Garcia-Tasende M S and Vazquez-Lopez E M 1997 *J. Chem. Soc., Dalton Trans.* 4289
34. Lobana T S, Sanchez A, Casas J, Garcia-Tasende M S and Sordo J S 1998 *Inorg. Chim. Acta* **267** 169
35. Lobana T S, Sanchez A, Casas J S, Castineiras A, Sordo J and Garcia-Tasende M S 1999 *J. Chem. Soc., Dalton Trans*. (submitted)