*Contribution from the Department of Chemistry,*
*University of Queensland, St. Lucia, Qld. 4067, Australia*

# Metal Complexes of Tridentate Hybrid Ligands. II.* Cobalt and Nickel Complexes of Ligands Containing the Donor Sequence As-N-S

**B. Chiswell[a] and K.W. Lee[b]**

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*Some nickel(II) and cobalt(II) complexes of six new hybrid tridentate ligands, all possessing the potential donor atom sequence of As–N–S, have been synthesised and studied. The ligands are of two types and were prepared by the condensation of* o-*dialkylarsinoanilines with*

(*i*) o-*methylthiobenzaldehyde.*

(*ii*)*2-thiophenaldehydes.*

*With type* (*i*) *ligands, complexes of formula* [*M ligand* $X_2$] (*where M = Co or Ni, X = anionic group*), *and* [*M*(*ligand*)$_2$]*Y* (*where M = Co or Ni, Y =* $ClO_4$ *or* $BPh_4$) *were obtained. In* [*Co ligand* $X_2$] (*where X = Br, I or* $NO_3$) *the ligand appears to act as a bidentate N–As ligand only. However, the* [*M*(*ligand*)$_2$]$^{2+}$ *cations appear to possess octahedral stereochemistry. The* [*Ni ligand·* $X_2$] *compounds are five-coordinate where X = Cl, Br or I, but octahedral where X = NCS. Ligands of type* (*ii*) *act as bidentate NAs ligands to give Ni*(*ligand*)$_2X_2$ *compounds. The nature of X determines whether such complexes are of high or low-spin tetragonal stereochemistry.*

## Introduction

Much interest has been shown, in recent years, in the complex compounds obtained from the interaction of cobalt(II) and nickel(II) salts with various tridentate ligands possessing donor atoms of markedly different ligand field strengths. In particular studies have concentrated upon the five-coordinate complexes from such hybrid ligands.[1,2]

In this work we report upon the cobalt(II) and nickel(II) complexes of six new tridentate ligands having the donor atom sequence As–N–S. All six ligands listed below were obtained by the condensation of *o*-dimethyl or *o*-diethyl-arsinoaniline[10] with the required aldehyde:

(i) N-(*o*-dimethylarsinophenyl)(*o*-methylthio)benzaldimine (I, MeSNAs).

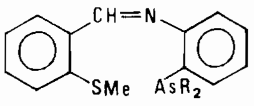
(ii) N-(*o*-diethylarsinophenyl)-(*o*-methylthio)benzaldimine (II, MeSNAsEt).

(iii) N-(*o*-dimethylarsinophenyl)-2-thiophenealdimine (III, TNAs).

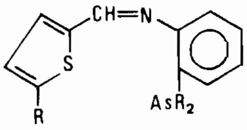
(iv) N-(*o*-diethylarsinophenyl)-2-thiophenealdimine (IV, TNAsEt).

(v) N-(*o*-dimethylarsinophenyl)-(4-methyl)-2-thiophenealdimine (V, MeTNAs).

(vi) N-(*o*-diethylarsinophenyl)-(4-methyl)-2-thiophenealdimine (VI, MeTNAsEt).

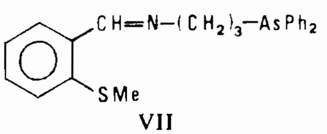


I, R=Me
II, R=Et



III, R=H, R′=Me
IV, R=H, R′=Et
V, R=Me, R′=Me
VI, R=Me, R′=Et

Sacconi *et. al.*[3] have previously studied the nickel(II) complexes of the tridentate ligand 1-(*o*-methylthiophenyl)-5-(diphenylarsino)-2-azapent-1-ene(VII), which also possesses an As–N–S donor atom sequence. High spin five-coordinate



VII

compounds of the type [Ni(ligand)$X_2$] (where X = Br or I) were obtained.

## Results

*Cobalt(II) Complexes* (see Table I). The interaction of equimolecular proportions of cobalt(II) salts with either of the ligands I or II yielded:

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* Part I. B. Chiswell and K.W. Lee, *Aust. J. Chem.*, *22*, 2315 (1969).

(a) All correspondence regarding this paper should be sent to this address.

(b) Present Address: Korea Institute of Science and Technology, Sungbook-ku, Seoul, Korea.

(1) L. Sacconi, J. Chem. Soc. (A), 248 (1970) and references therein.

(2) B. Chiswell, « The Chemistry of Multidentate Ligands Containing Heavy Group VB Donors », *Rewiews in Inorg. Chem.*, *1*, 1972. Ed. C.A. McAuliffe, Macmillan (to be published).

(3) L. Sacconi, G.P. Speroni, and R. Morassi, *Inorg. Chem.*, *7*, 1521 (1968).

**Table I.** Analytical data and physical properties of cobalt(II) complexes of MeSNAs and MeSNAsEt

| Complex | | Analysis (%) C | H | N | prepn[a] | $10^6\chi_g$ | Magnetic data[b] $10^6\chi_M'$ | $\mu_{eff}$(B.M.) | $\Lambda_M$[c] |
|---|---|---|---|---|---|---|---|---|---|
| Co(MeSNAs)$Br_2$1/2$H_2O$ | Found | 33.2 | 3.6 | 2.3 | EB-f-H | 13.53 | 8439 | 4.45 | 62 |
| | Calc. | 33.3 | 3.6 | 2.4 | | | | | |
| Co(MeSNAs)$(NO_3)_2$3$H_2O$ | Found | 34.0 | 4.3 | 7.8 | EBH-f-R(EB) | 13.33 | 7839 | 4.31 | 36 |
| | Calc. | 33.8 | 4.2 | 7.4 | | | | | |
| Co(MeSNAsEt)$I_2$ | Found | 32.4 | 3.3 | 2.0 | EB | 12.20 | 8580 | 4.52 | 30 |
| | Calc. | 32.1 | 3.3 | 2.2 | | | | | |
| [Co(MeSNAs)$_2$][Co(NCS)$_4$] | Found | 42.7 | 3.7 | 8.1 | E-BH | 10.70 | 11.330 | 2.78/4.00 | 62 |
| | Calc. | 42.7 | 3.6 | 8.3 | | | | | |
| [Co(MeSNAsEt)$_2$][Co(NCS)$_4$]3$H_2O$ | Found | 42.6 | 4.3 | 8.4 | E-f-R | 7.97 | 1548 | 1.89/4.00 | 62 |
| | Calc. | 42.8 | 4.5 | 7.5 | (C, Et) | | | | |
| [Co(MeSNAs)$_2$]$(ClO_4)_2$ | Found | 41.6 | 4.0 | 3.0 | E | 1.48 | 1789 | 2.08 | 160 |
| | Calc. | 41.7 | 3.9 | 3.0 | | | | | |
| [Co(MeSNAs)$_2$]$(BPh_4)_2$4$H_2O$ | Found | 67.3 | 5.7 | 1.9 | 2E | 6.00 | 9384 | 4.71 | 138 |
| | Calc. | 67.1 | 5.9 | 2.0 | | | | | |

[a] preparation method of the complex. [b] measured at 293°K. [c] measured in approx. $10^{-3}$ *M* nitromethane solution (cm$^{-1}$ ohm$^{-1}$ mole$^{-1}$).

(i) deep green Co ligand $X_2$ compounds (where ligand = MeSNAs or MeSNAsEt; X = (Cl), Br, I, NCS or $NO_3$.

(ii) greenish-brown compounds of the type [Co-(ligand)$_2$]$Y_2$ (where ligand = MeSNAs, Y = $ClO_4$ or $BPh_4$).

The bis-ligand complexes are crystalline and air-stable, but the monoligand compounds, especially the chlorides and nitrates are very hygroscopic. This property precluded reliable analysis of the chloro-compounds. All the compounds were very soluble without change in colour in acetone, and moderately soluble in other organic solvents.

The room temperature magnetic moments of the halide complexes, Co(MeSNAs)$Br_2$ . 3/2$H_2O$ and Co-(MeSNAsEt)$I_2$, have values of 4.45 and 4.52 B.M. respectively (see Table I). The molar conductivity of the halide complexes in nitromethane solution shows that they are appreciably dissociated, but the values obtained are much less than those of typical 1:1 electrolytes, suggesting that the halide ions are coordinated to cobalt(II).

The solid and solution spectra of halide complexes (Figure 1) in the visible region (830-400 nm) exhibit a structured absorption band in the region 800-625 nm. This band is very similar to that observed for the tetrahedral cobalt(II) complexes of the type $[CoX_4]^{2-}$, and this structured band can be assigned to the $\nu_3$ transition $^4A_2(F) \rightarrow {}^4T_1(P)$ for $T_d$ symmetry.

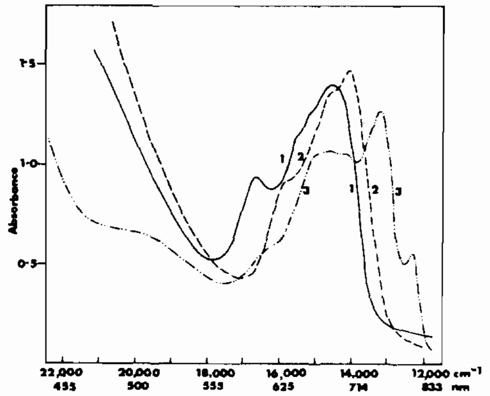

Figure 1. Visible spectra of Cobalt(II) halide complexes of MeSNAs in nitromethane solution (approx. $10^{-3}$ *M*). (1) Co(MeSNAs)$Cl_2$; (2) Co(MeSNAs)$Br_2$; (3) Co(MeSNAs)$I_2$.

On the basis of the conductivities and absorption spectra, it may be assumed that the terahedral configuraion can be achieved only if one of the potential donor atoms of the Schiff base does not form a bond to the metal ion. The thio-ether sulfur atom in the ligand donor atom sequence S–N–As is probably the unbonded atom because of its low donor power with respect to that of the nitrogen and arsenic atoms.

It has been reported that the analogous ligand MSBen-$NEt_2$ (derived from *o*-methylthiobenzaldehyde and N, N-diethylethylenediamine) forms high-spin complexes[4] of cobalt(II) salts of the general formula Co(MSBen-$NEt_2$)$X_2$ (X = Cl, Br, I) which have pseudotetrahedral stereochemistry with uncoordinated thio-ether groups both in the solid and solution; while the corresponding thiocyanate complex, Co(MeSBen-$NEt_2$)$(NCS)_2$, has been claimed to be a monomeric five-coordinate complex.

The nitrate complex, Co(MeSNAs)$(NO_3)_2$3$H_2O$, is very hygroscopic and slowly decomposes in nitromethane solution. Therefore reliable data from solid reflectance spectra and infrared spectra could not be obtained. But on the basis of the room-temperature magnetic moment (4.31 B.M.) and low conductivity ($\Lambda_M$ = 30), this nitrate compound has presumably the pseudo-tetrahedral configuration with the donor atom set $NAsO_2$ in the solid state.

The calculated magnetic moments of the thiocyanate complexes assuming the formula CoL$(NCS)_2$n$H_2O$ (L = MeSNAs, n = 0; L = MeSNAsEt, n = 3) were 3.65 and 3.38 B.M. respectively. These results do not compare with those expected for either high-spin or low-spin cobalt(II) complexes. Assuming the molecular formula, $[CoL_2][Co(NCS)_4]$, and taking 4.00 B.M. as the magnetic moment for the $[Co(NCS)_4]^{2-}$ anion, the calculated values for the magnetic moments of the cobalt(II) in the cations [Co-

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(4) L. Sacconi and G.P. Speroni, *Inorg. Chem.*, *7*, 295 (1968).

(MeSNAs)$_2$]$^{2+}$ and [Co(MeSNAsEt)$_2$]$^{2+}$ are 2.78 and 1.89 B.M. respectively. These values are within the ranges for low-spin cobalt(II) with square-planar and octahedral stereochemistry respectively. But the evidence for the stereochemistry based on magnetic moment measurements could not be substantiated by other physical measurements. The absorption spectra of these compounds could not give the characteristic patterns of the [CoL$_2$]$^{2+}$ cations in the visible region because of a strong charge transfer band and the strong absorption bands of the [Co(NCS)$_4$]$^{2-}$ anion (Figure 2).

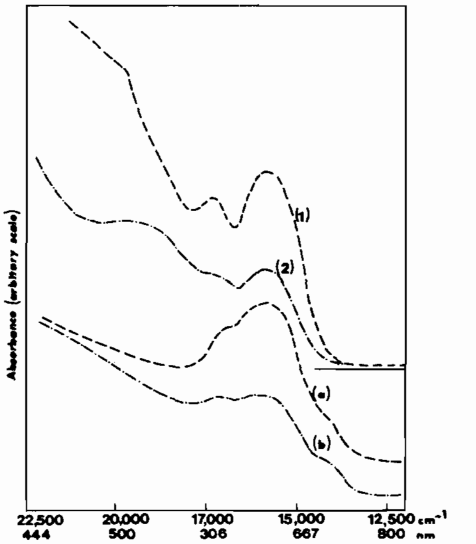

Figure 2. Visible spectra of Cobalt(II) thiocyanate complexes of MeSNAs and MeSNAsSt. Reflectance Spectra: (a) [Co(MeSNAs)$_2$][Co(NCS)$_4$] (b) [Co(MeSNAsEt)$_2$][Co(NCS)$_4$]. Solution spectra in MeNO$_2$: (1) compound (a), (2) compound (b).

The infrared spectra in the metal-sulfur stretching region show that the bis-ligand cobalt(II) complexes of the ligand MeSNAsEt exhibit a shoulder at ca. 359 cm$^{-1}$ which could be the Co–S stretching vibration, as has been observed in the corresponding nickel complexes (ν(Ni–S) = 345±5 cm$^{-1}$, and the analogous complexes[5] M(MeNNS)X$_2$ (ν(M–S) = 360±10 cm$^{-1}$; M = Mn$^{II}$, Fe$^{II}$, Co$^{II}$; MeNNS = N-(*o*-methylthiophenyl)pyridine-2-aldimine).

It may therefore be assumed that the cation [Co(MeSNAsEt)$_2$]$^{2+}$ has a low-spin octahedral stereochemistry with a magnetic moment of 1.80 B.M. with two tridentate ligands making up the donor atom set S$_2$N$_2$As$_2$. The compound [Co(MeSNAs)$_2$][Co(NCS)$_4$] exhibits no bands in the region 340-400 cm$^{-1}$, suggesting that the cation [Co(MeSNAs)$_2$]$^{2+}$ has presumably a square-planar stereochemistry with a magnetic moment of 2.78 B.M. and having the donor atom set N$_2$As$_2$.

The evidence for the presence of the [Co(NCS)$_4$]$^{2-}$ anion in these thiocyanate complexes is obvious from the physical measurements:

(i) absorption spectra in the visible region gave bands with the caracteristic shape and frequencies of the tethrahedral [Co(NCS)$_4$]$^{2-}$ anion[6] (Fig. 2).

(ii) the infrared spectra of the thiocyanate group[7] exhibits a strong broad band at 2070 (C-N stretching), a medium band at ca. 480 (N-C-S deformation), and a strong and broad band centred at 305-310 cm$^{-1}$ (Co-NCS stretching).

The bis-ligand complexes, Co(MeSNAs)$_2$Y$_2$nH$_2$O (Y = ClO$_4$, n = 0 ; Y = BPh$_4$, n = 4), are typical 1:2 electrolytes in nitromethane, and gave similar absorption spectra both in the solid and in nitromethane solution in the visible region. The perchlorate salt has a room-temperature magnetic moment of 2.08 B.M. and exhibits bands at 345 cm$^{-1}$ (medium) and 332 cm$^{-1}$ (strong) in the metal-sulfur stretching region,[8] suggesting that the perchlorate compound has a low-spin octahedral stereochemistry as has been observed in the cobalt(II complexes of analogous ligands with a donor set NNAs.[9]

The fact that the tetraphenylborate salt, [Co(MeSNAs$_2$](BPh$_4$)$_2$4H$_2$O is of the high spin type (4.71 B.M.) and the absence of the ν(Co-S) in the range 340-400 cm$^{-1}$ sould suggest that is has high-spin octahedral stereochemistry with two bidentate ligands and two water molecules in the first coordination sphere of cobalt(II).

## *Nickel(II) complexes*

The interaction of equimolecular quantities of nickel(II) halides and either of the ligands MeSNAs or MeSNAsEt, in ethanol or ethanol-benzene solution, yielded orange to dark brown solutions.

During refluxing of the solution, some insoluble hydrolyzed complex Ni(NAs)$_2$X$_2$ or Ni(NAsEt)$_2$X$_2$ (where X = Cl, Br, I; NAS = *o*-dimethylarsinoaniline)[10] was always isolated and had to be removed by filtration. The required complex compounds were obtained by addition of hexane to the filtrate, or by changing the solvent to n-butanol.

The chloride and bromide complexes of the ligand MeSNAsEt, which are very soluble in chloroform and can be recrystallized from chloroform\heptane, are very hygroscopic and take up moisture to change from a brown powder to a green oily mass. Other compounds shown in Table II are slightly hygroscopic, but are stable for long periods of time when stored in a dry atmosphere. They are very soluble in ethanol and moderately soluble in chloroform and nitromethane, but the solutions become turbid on standing.

Regarding the possibility[11] of an uncoordinated thioether sulfur donor atom, the far-infrared spectrum (250-400 cm$^{-1}$) shows a relatively sharp and medium band around 340-350 cm$^{-1}$ which is absent in ana-

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(5) P.S.K. Chia and S.E. Livingstone, *Aust. J. Chem.*, *22*, 1611 (1969).

(6) F.A. Cotton, D.M.L. Goodgame, M. Goodgame, and A. Sacco, *J. Amer. Chem. Soc.*, *83*, 4157 1(961).

(7) A. Sabatini and I. Bertini, *Inorg. Chem.*, *4*, 959, 1665 (1965).

(8) D.M. Adams, « Metal-ligand and Related Vibrations », Edward Arnold, London, 1967, p. 319; D.M. Adams and J.B. Correll, *J. Chem. Soc.* (*A*), 1299 (1968); I. Ojima, T. Inamato, T. Onishi, N. Inamato, and K. Tamaru, *Chem. Comm.*, 1501 (1969).

(9) K.W. Lee, Ph.D. Thesis, University of Queensland, 1971 (to be published).

(10) B. Chiswell and K.A. Verrall, *J. prakt. Chem.*, *312*, 751 (1970).

(11) L. Sacconi and R. Morassi, *J. Chem. Soc.* (*A*), 575 (1970; S.E. Livingstone, *Quart. Revs.*, *19*, 386 (1965) and references therein.

**Table II.** Analytical Data of Nickel(II) Complexes of Ligands Containing Donor Atom Sequences S-N-As.

| Complex | | Analysis (%) | | | | prepn. * |
|---|---|---|---|---|---|---|
| | | C | H | N | Ni | |
| $Ni(MeSNAs)Cl_2 1\frac{1}{2}H_2O$ | Found | 39.1 | 4.4 | 3.1 | 11.8 | |
| | Calc. | 39.3 | 4.3 | 2.9 | 12.0 | |
| $Ni(MeSNAs)Br_2BuOH$ | Found | 38.4 | 4.2 | 2.4 | | E-f-Bu |
| | Calc. | 38.4 | 4.6 | 2.2 | | |
| $Ni(MeSNAs)I_2EtOH$ | Found | 31.4 | 3.4 | 2.3 | 8.6 | EB-f-HEt |
| | Calc. | 31.3 | 3.5 | 2.0 | 8.5 | |
| $Ni(MeSNAs)(NCS)_2\frac{1}{2}H_2O$ | Found | 42.0 | 3.7 | 8.4 | | EBu |
| | Calc. | 41.9 | 3.7 | 8.2 | | |
| $Ni(MeSNAs)_2(ClO_4)_2$ | Found | 41.6 | 3.9 | 3.0 | | EBu |
| | Calc. | 41.7 | 3.9 | 3.0 | | |
| $Ni(MeSNAs)_2(BPh_4)_2H_2O$ | Found | 69.5 | 5.5 | 2.3 | | 2E |
| | Calc. | 69.6 | 5.7 | 2.0 | | |
| $Ni(MeSNAsEt)I_2$ | Found | 31.9 | 3.5 | 2.4 | | EB-f-R(CE) |
| | Calc. | 32.1 | 3.3 | 2.2 | | |
| $Ni(MeSNAsEt)(NCS)_2$ | Found | 45.0 | 4.6 | 8.6 | | EB-Bu |
| | Calc. | 44.9 | 4.1 | 7.9 | | |
| $Ni(MeTNAs)_2Br_23H_2O$ | Found | 37.4 | 4.0 | 3.6 | 7.0 | EB-f |
| | Calc. | 38.0 | 4.3 | 3.2 | 6.7 | |
| $Ni(MeTNAs)_2I_2$ | Found | 36.8 | 3.1 | 3.0 | 6.3 | E-f |
| | 36.4 | 36.4 | 3.5 | 3.0 | 6.4 | |
| $Ni(TNAsEt)_2(NCS)_2\frac{1}{2}EtOH$ | Found | 47.6 | 4.8 | 6.3 | | EB-E |
| | Calc. | 47.8 | 4.7 | 6.8 | | |
| $Ni(MeTNAsEt)_2(NCS)_2$ | Found | 48.1 | 4.9 | 6.5 | 6.9 | 2EB |
| | Calc. | 48.5 | 4.8 | 6.7 | 7.0 | |
| $Ni(MeTNAsEt)_2(ClO_4)_22H_2O$ | Found | 39.8 | 4.5 | 2.9 | 6.2 | 2EB |
| | Calc. | 40.0 | 4.6 | 2.9 | 6.1 | |

* prepn. Method of preparation of the complex.

**Table III.** Physical properties of nickel(II) complexes of ligands containing the donor atom sequence S-N-As.

| Complex | Magnetic data * | | | | State | Frequency ($10^3cm^{-1}$=kK) |
|---|---|---|---|---|---|---|
| | $10^6\chi_g$ | $10^6\chi_M'$ | $\mu_{eff}$(B.M.) | $\Lambda_M$ ** | | |
| $Ni(MeSNAs)Cl_2 1\frac{1}{2}H_2O$ | 10.2 | 4830 | 3.38 | 6.3 | solid | 14.5, 20.0, ~26 |
| | | | | | $MeNO_2$ | 14.0, 20.0 |
| $Ni(MeSNAs)Br_2BuOH$ | | | | | solid | 14,4, 19.0 |
| $Ni(MeSNAs)I_2EtOH$ | 5.42 | 4067 | 3.10 | 38.4 | solid | 14.2, 18.0sh, 22.5 |
| | | | | | $MeNO_2$ | 14.2, 18.0, 21.5sh, 23.5sh |
| $Ni(MeSNAs)(NCS)_2\frac{1}{2}H_2O$ | 7.37 | 3984 | 3.09 | i.s. | solid | 11.0, 16.0sh, 20.0sh |
| $Ni(MeSNAs)_2(ClO_4)_2$ | 4.05 | 41.83 | 3.17 | 167 | solid | 12.0, 20.0sh |
| $Ni(MeSNAs)_2(BPh_4)_2H_2O$ | 2.82 | 4550 | 3.28 | 133 | solid | 12.0, 18.0sh, 20.0sh, 24.0 |
| $Ni(MeSNAsEt)I_2$ | 5.57 | 4060 | 3.11 | | solid | 13.5, 16.5, 20.5 |
| | | | | | $MeNO_2$ | 14.0, 18.0, 24.0 |
| $Ni(MeSNAsEt)(NCS)_2$ | 7.06 | 4044 | 3.11 | i.s. | solid | ~11.0, 16.5sh, 20.0, 25.0 |
| $Ni(MeTNAs)_2Br_23H_2O$ | 0.774 | 1079 | 1.60 | 30.1 | solid | 17.5, 24.0 |
| $Ni(MeTNAs)_2I_2$ | diamagnetic | | | 74.3 | solid | 16.5, 21.3, 25.0 |
| $Ni(TNAsEt)_2(NCS)_2\frac{1}{2}EtOH$ | diamagnetic | | | i.s. | solid | 19.0, 24.0 |
| $Ni(MeTNAsEt)_2(NCS)_2$ | diamagnetic | | | i.s. | solid | 19.5, 23.5 |
| $Ni(MeTNAsEt_2(ClO_4)_22H_2O$ | diamagnetic | | | 180 | solid | 19.5, 23.5 |
| | | | | | $MeNO_2$ | 20.0 |

* measured at 295°K. ** measured in ca. $10^{-3}$ *M* nitromethane solution. i.s. insufficiently soluble, sh shoulder.

logous ligands containing NNAs donor atoms and in some cobalt(II) complexes of the ligand MeSNAs for which a tetrahedral configuration has been assigned above on the basis of their physical properties.

Metal-sulfur stretching frequencies[8] lie in the range 480-210 $cm^{-1}$. In the monothio-β-diketonate complexes, metal-sulfur stretching frequencies[12] are in the range 400-360 $cm^{-1}$ whereas the metal-sulfur frequencies for the complexes[5] $M(SNN)X_2$ (M = Mn to Cu; X = Cl, Br or I; SNN = tridentate donor sequence) occur in a narrower range, viz 360±10 $cm^{-1}$. Thus the band at ca. 350 $cm^{-1}$ appearing in the spectra of all nickel(II) complexes may be assigned as ν(M-S), suggesting that the ligand with SNAs donor set must be functioning as a tridentate chelating agent.

The room temperature magnetic moments of the solid compounds are reported in Table III, and show that the complexes are all of the high-spin type.

The reflectance spectra (Figure 3) of the halogen complexes recorded in the region 830-400 nm, are very similar and display bands at 715-685 nm and at about 500 nm. The slight differences in the absorption maxima can be correlated with the position of the halogen in the spectrochemical series. Therefore, it can be concluded that the nickel halides all possess essentially the same stereochemistry in the

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(12) S.H.H. Chaston and S.E. Livingstone, *Aust. J. Chem.*, *20*, 1965 (1967).

solution which explains the relatively high molar conductivities of the iodide complexes:

$$[Ni(MeSNAs)_2] \leftrightharpoons [Ni(MeSNAs)I] + I^-$$

It is interesting to note that the analogous complexes $Ni(MeSNNEt)X_2$ (X = halogen; MeSNNEt = N-(N′.N′-diethylene)-*o*-methylthiobenzaldimine) give rise to a temperature-dependent equilibrium between five-coordinate and tetrahedral forms in *o*-dichlorobenzene.[13]

Thus it can be concluded that in these halide complexes the rigid S-N-As donor sequence have five-coordinate stereochemistry in the solid state, whereas in nitromethane solution they give rise to an equilibrium between five-coordinate and square-planar species.

The thiocyanate and perchlorate compounds are readily formed from the corresponding ligands in ethanol-butanol solvent. The tetraphenylborate salt was prepared by the addition of lithium tetraphenylborate solution to the solution which contained a 2:1 molecular ratio of the ligand to nickel(II) chloride. The bis-ligand perchlorate and tetraphenylborate complexes are soluble in common organic solvents such as acetone, ethanol and nitromethane but the thiocyanate complexes are not soluble enough in nitromethane to allow for the measurement of conductivity values. The bis-ligand complexes exhibit typical 1:2 electrolyte behaviour in nitromethane. All the complexes are of the paramagnetic type in the solid state, with magnetic moments ranging from 3.09 to 3.28 B.M. (see Table III).

The patterns of reflectance spectra are much the same for both the mono-ligand thiocyanate and bis-ligand perchlorate complexes (Figure 3). They exhibit bands at about 910 and 625 nm in the case of thiocyanate complexes, whilst the bis-ligand perchlorates display only the band at 830-900 nm both in the solid state and in nitromethane solution. The higher energy band is probably hidden beneath the intense charge transfer bands. These spectra are comparable to those exhibited by other transfer bands. These spectra are comparable to those exhibited by other six-coordinate octahedral nickel(II) complexes having the corresponding anions.

There is some evidence of a shift in the maxima of the absorption bands of the bis-ligand ćomplexes in comparison with those of the thiocyanate, and this may be attributed to the different donor sets; *i.e.* $N_3S_2As$ in thiocyanate complexes and $N_2S_2As_2$ in the bis-ligand complexes.

Other evidence for the octahedral configuration of the thiocyanate complexes is provided by the infrared spectra in the C-N stretching region. These display two bands at 2070-2088 $cm^{-1}$ and 2122-2128 $cm^{-1}$, suggesting that two kinds of thiocyanate groups *i.e.* N-bonded terminal thiocyanate and bridging thiocyanate[14] are present in these compounds, as has already been observed in other thiocyanate complexes.

The absorption spectra of these complexes in nitromethane (Figure 4) generally exhibit the same patterns as other five-coordinate complexes, but the bands at about 1200 and about 715 nm in the iodide complexes arc almost collapsed and these spectra show no other bands below 1000 nm except for a band at 1040 nm which is presumably spin-forbidden as indicated by its very sharp weak nature. This might be indicative of the presence of an equilibrium between a five-coordinate and a dissociated square-planar system in the solid state and may be assigned a five- coordinate stereochemistry in this state, on the basis of the similarity of their spectra to those of other nickel(II) halide complexes of the NNAs donor ligands.[9]

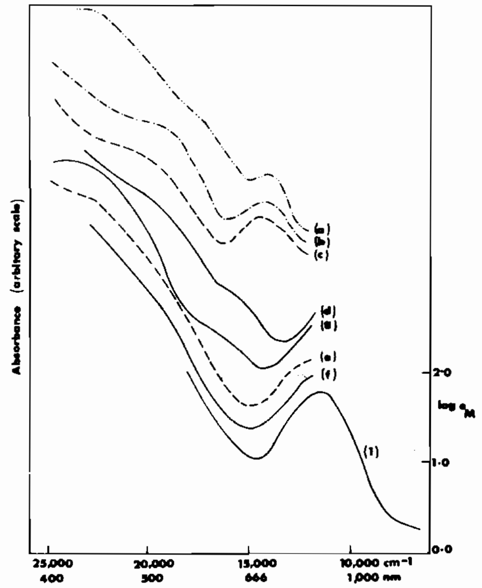

Figure 3. Spectra of Nickel(II) complexes of MeSNAs. Reflectance spectra: $Ni(MeSNAs)X_2$ (a) X=I, (b) X=Br, (c) X=Cl, (d) X=NCS; $Ni(MeSNAs)_2Y_2$ (e) $Y=BPh_4$, (f) $Y=ClO_4$, (g) $Ni(MeSNAsEt)(NCS)_2$. (1) Solution spectrum of (f) in $MeNO_2$.

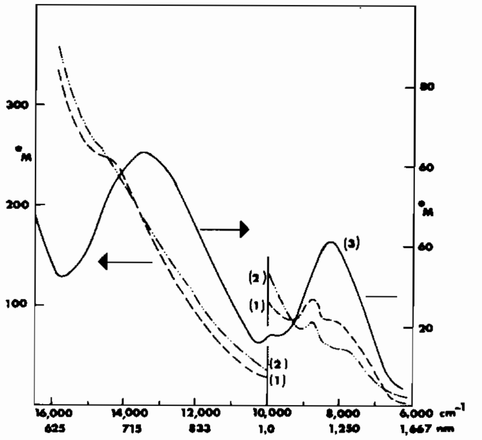

Figure 4. Solution of Nickel(II) iodide complexes of ligands MeSNAs and MeSNAsEt in nitromethane. (1) $Ni(MeSNAs)I_2$, (2) $Ni(MeSNAsEt)I_2$, (3) $Ni(Me_2NNAs)Br_2$ in $MeNO_2$ (right hand scale).

The interaction of nickel(II) salts with the (appropriate) ligands derived from *o*-dialkylarsinoalines and

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[13] L. Sacconi and P.G. Speroni, *Inorg. Chem.*, 7, 295 (1968).
[14] D.C.M. Mitchell and R.J.P. Williams, *J. Chem. Soc.*, 1912 (1960).

2-thiophenealdehyde or its 5-methyl derivative in ethanol-benzene solution leads to no appreciable colour change in solution. Upon slow evaporation of solvent in a rotary-evaporator, the yellow-green solution changes in colour to deep red-brown during evaporation and red crystals separate.

It should be noted that the complexes Ni(MeTNAs)$_2$X$_2$ (X = Br, I) are deep blue and dark yiellow, respectively, and much more intense in colour than the corresponding Ni(NAs)$_2$X$_2$ complexes.[15]

The thiocyanate complexes are insoluble in nitromethane, but dissolve in ethanol to give a green solution. Upon evaporation dark red-brown crystals are obtained. This may be taken to indicate that the thiocyanate complexes are present as a six-coordinate solvated species in ethanol solution.

The room-temperature magnetic moments of all these solid compounds show that they are of the low-spin, diamagnetic type, except for Ni(MeTNAs)$_2$Br$_2$-3H$_2$O which has an anomalous magnetic moment of 1.60 B.M.

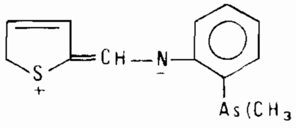
The infrared spectra of the C=N stretching region, 1700-1500 cm$^{-1}$, and anions are tabulated in Table III. Holm et al.[16], in a comprehensive review of investigations on Schiff base ligands, noted that the C=N frequencies of the metal Schiff base complexes are only slightly changed compared to the free ligand, and that nearly all lie in the 1605-1640 cm$^{-1}$ range.

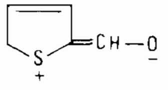
Uncomplexed ligands containing thiophene entities,[17] N-methyl-2-thiophenealdimine and bis(2-thiophenaldehyde)ethylenediamine exhibit C=N stretching frequencies at 1647 and 1635 cm$^{-1}$, respectively. Chelation involving the conjugated C=N group results in a shift by about 20 cm$^{-1}$ to 1609-1628 cm$^{-1}$ from those of the free ligands.

The complexes listed in Table 4 exhibit no bands above 1610 cm$^{-1}$ and strong bands in the region 1589-1610 cm$^{-1}$ and 1570 ± 5 cm$^{-1}$.

The former band (1600 ± 10 cm$^{-1}$) is presumably associated with the stretching vibration of the conjugated C=N group coordinated to the metal ion, suggesting that the ligand containing the TNAs donor set is at least operating as a bidentate ligand. Evidence that the thiophene sulfur atom is coordinated to the nickel(II) atom could not be obtained.

However, the nature of the weak donor properties of thiophene sulfur atoms has been demonstrated in the metal complexes containing the thiophene nuclues.[17,18] The electron distribution of TNAs may be considerably affected by pi-electron delocalization associated with the contribution of a highly polar resonance form,





The lower electron density on the sulfur atom resulting from resonance of the type illustrated above weakens the donor properties of the sulfur atom as in 2-thiophenaldehyde.[17]

The reflectance spectra of the halide compounds, Ni(MeTNAs)$_2$X$_2$·nH$_2$O (X = Br, n = 3; X = Cl, n = O), are different to those of the thiocyanate and perchlorate complexes (Figure 5).

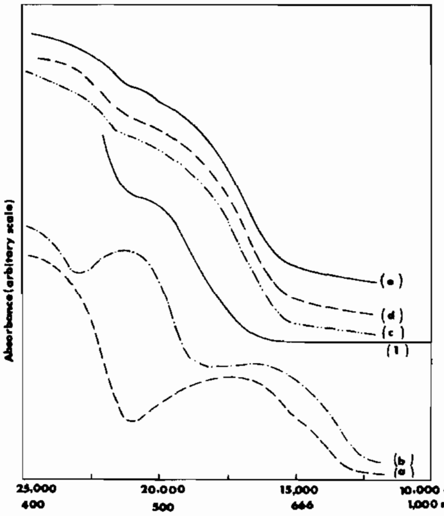


Figure 5. Visible spectra of Nickel(II) complexes of TNAs derivatives. Reflectance spectra (a) Ni(MeTNAs)$_2$Br$_2$3H$_2$O, (b) Ni(MeTNAs)$_2$I$_2$, (c) Ni(TNAsEt)$_2$(NCS)$_2$½EtOH, (d) Ni(MeTNAsEt)$_2$(NCS)$_2$, (e) Ni(MeTNAsEt)$_2$(ClO$_4$)$_2$2H$_2$O. Solution spectrum in nitromethane (1) Ni(MeTNAsEt)$_2$-(ClO$_4$)$_2$ . 2H$_2$O.

The bromide complex displays a very broad band centred at 570 nm and amuch more intense band at about 415 nm in the solid state. The latter band is presumably the charge transfer band. The molar conductivity in nitromethane solution indicates an appreciable dissociation and shows values of about 30 which are less than 40% of a typical 1: 1 electrolyte in this solvent. This suggests that the bromide ions are coordinated to the nickel atom.

From the above arguments based on infrared results, molar conductivities and low magnetic moments (1.60 B.M.) in the solid state, it is likely that Ni(MeTNAs)$_2$Br$_2$3H$_2$0 has either a six-coordinate tetragonal configuration which gives rise to an intermediate room-temperature magnetic moment, or a mixture of species with different geometries.

The iodide compound, Ni(MeTNAs)$_2$I$_2$ is diamagnetic in the solid state and a typical 1: 1 electrolyte in nitromethane. It exhibits a reflectance spectrum with a similar pattern to that of the corresponding bromide complex, but gives another strong band at 470 nm.

In particular, the bands at approx. 625 and 470 nm for Ni(MeTNAs)$_2$I$_2$ can be correlated with those at 610-620 ($\varepsilon_M$ = 1000-2000) of low-spin five-coordinate complexes, [Ni(diars)$_2$X]Y (X = halogen, NCS etc.; Y = X or ClO$_4$; diars = *o*-phenylenebis(dimethylarsine) if the different donor atom set (N$_2$As$_2$I)

(15) B. Chiswell, R.A. Plowman, and K.A. Verrall, *Inorg. Chim. Acta*, accepted for publication, 1973.

(16) R.H. Holm, G.V. Everett Jr., and A. Chakravorty, *Prog. Inorg. Chem.*, *7*, 161 (1966).

(17) M.P. Coakley, L.H. Young, and R.A. Gallagher, *J. Inorg. Nucl. Chem.*, *31*, 1449 (1969).

(18) G.L. Eichhorn and J.C. Bailar Jr., *J. Amer. Chem. Soc.*, *75*, 2905 (1953).

**Table IV.** Infrared Spectral Data.

| (a) C-N stretching region (1600-1700 cm$^{-1}$) of nickel(II)-TNAs derivatives | | |
|---|---|---|
| Complex | Absorption band maxima (cm$^{-1}$) | |
| $Ni(MeTNAs)_2Br_23H_2O$ | 1610vs, 1570s | |
| $Ni(MeTNAs)_2I_2$ | 1609vs, 1575s | |
| $Ni(TNAsEt)_2(NCS)_2½EtOH$ | 1608s, 1568s, 1518m | |
| $Ni(MeTNAsEt)_2(NCS)_2$ | 1605s, 1563s, 1540w | |
| (b) Thiocyanate group | | |
| | $\nu$(C-N) | $\delta$(NCS) |
| $Ni(MeSNAs)(NCS)_2½H_2O$ | 2122s, 2070s | 470m |
| $Ni(MeSNAsEt)(NCS)_2$ | 2128s, 2088vs.br | 470s |
| $Ni(MeTNAsEt)_2(NCS)_2$ | 2110vs | 470w, 417s |
| $Ni(MeTNAsEt)_2(NCS)_2$ | 2090vs | 467w, 415s |
| (c) Perchlorate group | | |
| $Ni(MeSNAs)_2(ClO_4)_2$ | 1090vs.br | 626s |
| $Ni(MeTNAsEt)_2(ClO_4)_22H_2O$ | 1090vs.br | 627s |

in the $Ni(MeTNAs)_2I_2$ complex is taken into account. Furthermore, the calculated nucleophilic reactivity constant ($\Sigma n^{\circ}$ = 28.37) for the donor atom set $N_2As_2I$ also falls within the range ($\Sigma n'$ = 25.5-37.2) found for low-spin five-coordinate nickel(II) complexes.[1]

Therefore the bands at 625 nm and 470 nm for the iodide complex can be assigned as transitions, $\nu_1(^1A_1 \rightarrow {}^1B_1)$ and $\nu_2(^1A_1 \rightarrow {}^1E)$ respectively, and the transition $\nu_3(^1A_1 \rightarrow {}^1A_2)$, which is observed at approx. 385 nm ($\varepsilon_M$ = 100-300) for $[Ni(diars)_2X]Y$, is presumably obscured by the charge transfer band. However, the possibility that $Ni(MeTNAs)_2I_2$ is a diamagnetic, strongly tetragonally distorted compound, cannot be categorically dismissed.

The reflectance spectra of the thiocyanate complexes, $NiL(NCS)_2$ (L = TNAsEt, MeTNAsEt) show essentially the same pattern as that of the perchlorate complex, $Ni(MeTNAsEt)_2(ClO_4)_23H_2O$, and are different to the halide complexes $Ni(MeTNAs)_2X_2$.

The thiocyanate and perchlorate complexes are all diamagnetic at room temperature. The thiocyanate complexes are not sufficiently soluble in a non-coordinating solvent such as nitromethane to allow for the measurement of the conductivity and solution spectra On the other hand the perchlorate is a typical 2: 1 electrolyte in nitromethane and displays one band at about 485 nm and no appreciable absorption below 590 nm in the same solvent.

This may suggest that the perchlorate complex has a square-planar configuration in both solid state and solution, and possibly the same stereochemistry occurs in the thiocyanate complexes.

The infrared spectrum of perchlorate complexes displays a very strong and broad band at 1090 cm$^{-1}$ and a sharp and strong band at 627 cm$^{-1}$, indicating that the perchlorates are un-coordinated ionic groups.[19]

However, thiocyanate complexes exhibit a strong peak at 2092 or 2100 cm$^{-1}$ in the C-N stretching frequency region. The values are much higher than those found in monomeric N-bonded thiocyanate and also in ionic thiocyanate groups and they are comparable to those found for the S-bonded thiocyanate [$\nu_1$(C-N) = 2080-2120 cm$^{-1}$].[20,21]

Furthermore, the N-C-S bending modes are observed as a strong peak at approx. 416 cm$^{-1}$ and a weaker band at 467 cm$^{-1}$ which may also indicate an S-bonded thiocyanate group, but assignment in the C-S stretching region could not be made because the region is not completely free of ligand absorption (see Table IV).

On the basis of the above argument, is seems not unreasonable to suggest that the diamagnetic thiocyanate complexes have a six-coordinate strongly tetragonally distorted stereochemistry, in which two thiocyanate groups occupy *trans*-position bonding through the sulfur atom.

## Experimental Section

### *General procedure for the preparation of metal complexes*

The warm and deaerated ligand solution was slowly added to the appropriate hot metal salt solution (code (i)) in approx. 40 ml of absolute ethanol or mixed solvent (code (ii)).

(i) When the metal complex compound separated during refluxing of the solution for 20 min. it was digested for another 10-20 minutes and the solution was then allowed to cool to room temperature.

(ii) When the metal complex compound did not appear to separate within approx. 20 min., the solvent was slowly evaporated until crystals started to separate, or evaporated to approx. 20 ml, and allowed to cool either to room temperature, or in an ice-bath.

(iii) When procedure (ii) did not yield the desired metal complex, the solution was warmed and another solvent (10-40 ml) slowly added followed by procedure (i) or (ii).

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(19) D.A. Baldwin and G.J. Leigh, *J. Chem. Soc. (A)*, 1431 (1968) and references therein.

(20) « Specialist Periodical Reports », *I*, pp. 195-199, and references therein. Ed. N.N. Greenwood, Chem. Soc., London, 1970.

(21) R.J.M. Clark and C.S. Williams, *Spectrochim. Acta*, *22*, 1081 (1966).

The metal complexes were collected and washed with appropriate solvents and finally with hexane. If necessary, the metal complex compounds were recrystallized from the appropriate solvent. When undesired products or impurities separated during the procedure (i), (ii) or (iii), the solution was filtered while hot.

*Code* (i): (a) The number in front of the solvent indicates mole ratio of the ligand and metal salt; no arabic number indicates 1:1 mole ratio; (b) f: filtered while hot; (c) R(   ): recrystallized from solvents in the bracket; (d): change of solvent.

(ii) The code for solvents used for the preparation and the recrystallization of the complex compounds is as follows: Bu 1-butanol; E ethanol; Et diethyl ether; B benzene; C chloroform; H hexane; D dichloromethane.

(iii) Examples of the codes for the preparation of metal complexes: (a) EBu-F: 1:1 mole ratio of ligand and metal salt was used in a mixed solvent of absolute ethanol and n-butanol and filtered while hot to remove the undesired products; (b) 2E-R(Et): The complex compounds are prepared from a 2:1 mole ratio of ligand to metal salt in ethanol solution and recrystallized from ethanol; (c) E($NO_3$+$BPh_4$): A tetraphenylborate salt was added to equimolecular quantities of metal(II) nitrate and ligand in ethanol.

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