Inorganica Chimica Acta, 18 (1976) 35–45

Syntheses and Spectral Study of New Iodobis(dialkyldithiocarbamate) Complexes of Arsenic, Antimony and Bismuth.*

C. A. TSIPIS and G. E. MANOUSSAKIS**
Laboratory of Inorganic Chemistry, University of Thessaloniki, Thessaloniki, Greece
Received September 1, 1975

Fifteen new iodobis(dialkyldithiocarbamate) complexes of arsenic, antimony and bismuth have been prepared by reacting the corresponding tris(dialkyldithiocarbamates) with iodine. A possible mechanism of the reaction has been proposed. The new complexes have been characterized by elemental analysis, molecular weights, and their i.r., ^{1}H n.m.r., electronic and mass spectra. The spectral data are discussed in relation to structures and compared to those of the corresponding tris(dialkyldithiocarbamate) complexes. Some structural conclusions have been also drawn for these new complexes based upon the spectral studies. Furthermore, the effects of the presence of iodine, of the electron releasing ability of the amine group and of the nature of the metal atom on certain characteristic features of their structures have been studied.

Introduction

In the last few years a number of studies have been carried out on the reactions between halogens and dithiocarbamate complexes of the transition and non-transition metals.[1–12]

In most cases oxidative addition reactions take place to yield halogeno–dithiocarbamate complexes in which the metal atom appears in an unusually high oxidation number.[1–7] This fact indicates that the dithiocarbamate ligands stabilize the central atom in higher oxidation states.

In some cases, however, only oxidation reactions take place in which the dithiocarbamate ligands are oxidized to thiuramdisulfides producing thiuramdisulfide complexes.[4]

Of special interest is the Willemse and Steggerda[8] observation that the reactions between halogens and diethyldithiocarbamate complexes of iron(III), cobalt(III), antimony(III) and copper(II) result in the oxidation of the metal atom as well as of the dithiocarbamate ligand.

Finally, there are a few cases where, by reacting halogens with dithiocarbamate complexes, only substitution reactions take place and the metal atom maintains its oxidation number.[10–12]

Considering the above observations, we thought it would be advisable to do a systematic study of the reactions between the dithiocarbamate complexes of As(III), Sb(III) and Bi(III) as prepared in this laboratory[13] and the halogens. The present work involves the reaction of tris(dialkyldithiocarbamate) complexes of arsenic, antimony and bismuth with iodine. Fifteen new iodobis(dialkyldithiocarbamate) complexes of the general formula $IM(R_2dtc)_2$ were prepared (wherein the dithiocarbamato group = R_2dtc, R = Et, i-Bu or Bz and R_2 = $(CH_2)_4$ or $(CH_2)_5$ abbreviated as Pyrr and Pip respectively and M = As, Sb or Bi).

The structure of these complexes was studied spectroscopically by means of their i.r., ^{1}H n.m.r., electronic and mass spectra, and their properties are compared to those of the corresponding tris(dialkyldithiocarbamate) complexes.

Results and Discussion

When to a solution of the tris(dialkyldithiocarbamate) complex of arsenic, antimony or bismuth a solution of iodine is added, under defined proportion and at normal temperature, a reaction takes place in which one of the three dithiocarbamate ligands is substituted by an iodine atom. The products of the reaction are the iodobis(dialkyldithiocarbamate) complexes of the metals and the corresponding tetraalkylthiuramdisulfides.

By this reaction fifteen new iodobis(dialkyldithiocarbamate) complexes were prepared. All are crystalline compounds which are stable to the atmosphere. The analytical data for the compounds, their colours, melting points and yields are shown in Table I.

---

* Taken in part from the Ph. D. Thesis of C. A. Tsipis, University of Thessaloniki, 1974.

** Author to whom inquiries should be directed.

TABLE I. Analytical and Physical Data.[a]

Compound	Color	Yield (%)	M.P. °C	% C	% N	% H	% S	% I	% M[b]	M.W.
$IAs(Et_2dtc)_2$	Yellow	75	153–155	24.02 (24.10)	5.58 (5.62)	4.04 (4.04)	26.0 (25.74)	24.5 (25.46)	14.8 (15.03)	502 (498.4)
$ISb(Et_2dtc)_2$	Yellowish	73	155–156	22.06 (22.03)	5.23 (5.14)	3.65 (3.70)	24.2 (23.52)	22.6 (23.28)	21.7 (22.33)	541 (545.2)
$IBi(Et_2dtc)_2$	Yellow	85	159–160	19.09 (18.99)	4.40 (4.43)	3.15 (3.19)	21.2 (20.28)	19.2 (20.07)	32.8 (33.04)	872 (632.4)
$IAs(i\text{-}Bu_2dtc)_2$	Yellowish	65	149–150	35.46 (35.42)	4.58 (4.58)	5.93 (5.89)	19.8 (21.01)	19.2 (20.79)	11.8 (12.27)	616 (610.2)
$ISb(i\text{-}Bu_2dtc)_2$	Yellowish	72	153–154	33.14 (32.90)	4.17 (4.26)	5.40 (5.47)	20.7 (19.51)	18.2 (19.31)	17.9 (18.52)	648 (657.1)
$IBi(i\text{-}Bu_2dtc)_2$	Yellow	80	143–144	29.20 (29.04)	3.76 (3.76)	4.81 (4.83)	16.8 (17.22)	16.5 (17.04)	28.2 (28.07)	1038 (744.3)
$IAs(Bz_2dtc)_2$	Orange	52	124–138d[c]	48.32 (48.27)	3.82 (3.75)	3.79 (3.75)	17.8 (17.18)	16.3 (17.00)	9.9 (10.03)	762 (746.4)
$ISb(Bz_2dtc)_2$	Orange	64	84–89d	45.88 (45.42)	3.51 (3.53)	3.56 (3.53)	16.7 (16.16)	15.3 (15.99)	15.7 (15.34)	796 (793.2)
$IBi(Bz_2dtc)_2$	Yellow	75	86–105d	40.87 (40.92)	3.14 (3.18)	3.09 (3.18)	14.0 (14.56)	13.8 (14.41)	24.0 (23.73)	1258 (880.4)
$IAs(Pyrrdtc)_2$	Yellowish	68	215–219d	23.96 (24.30)	5.62 (5.66)	3.23 (3.23)	26.2 (25.95)	24.9 (25.67)	14.9 (15.16)	489 (494.2)
$ISb(Pyrrdtc)_2$	Yellowish	80	251–254d	21.90 (22.20)	5.09 (5.17)	3.01 (2.95)	24.3 (23.70)	22.7 (23.45)	21.6 (22.50)	534 (541.0)
$IBi(Pyrrdtc)_2$	Yellow	84	263–265d	19.66 (19.11)	4.58 (4.45)	2.67 (2.54)	19.8 (20.41)	19.5 (20.19)	32.9 (33.26)	695 (628.2)
$IAs(Pipdtc)_2$	Yellowish	76	214–216d	27.52 (27.59)	5.32 (5.36)	3.87 (3.83)	25.1 (24.55)	23.5 (24.30)	14.0 (14.34)	527 (522.2)
$ISb(Pipdtc)_2$	Yellowish	82	244–245d	24.98 (25.32)	4.89 (4.92)	3.48 (3.51)	23.0 (22.53)	21.6 (22.30)	20.9 (21.40)	562 (569.0)
$IBi(Pipdtc)_2$	Yellow–Orange	88	243–245d	22.06 (21.96)	4.18 (4.26)	3.05 (3.04)	18.9 (19.54)	18.7 (19.33)	31.9 (31.84)	793 (656.2)

[a] Figures in parentheses are the calculated values. [b] M = As, Sb or Bi. [c] d = decomposition.

The overall reaction for the preparation of the compounds may be represented by the following general equation:

$$[R_2N(S)CS]_3M + \frac{1}{2} I_2 \rightarrow [R_2N(S)CS]_2MI + \frac{1}{2}[R_2NCSS]_2$$

In this reaction, possibly, dithiocarbamate radicals are formed through an homolytic rupture of M–S bonds, which, in succession, are dimerized into tetraalkylthiuramdisulfides. This seems likely, because it is well known that the tetraalkylthiuramdisulfides and the corresponding free dithiocarbamate radicals are in equilibrium in solution.[14]

Under the experimental conditions, though at times an excess of iodine was used (two-fold of the required quantity), the isolated products were always iodobis (dialkyldithiocarbamate) complexes. The facile substitution of one of the three dithiocarbamate ligands of the tris(dialkyldithiocarbamate) complexes of arsenic, antimony and bismuth by an iodine atom shows that one of the three ligands is more weakly bonded to the central atom. This fact has already been ascertained by spectroscopic studies of these complexes[13,15] as well as by X-ray data for the tris(diethyldithiocarbamato) arsine.[16]

I.r. Spectra

Table II shows the most relevant bands together with the bonds to which these bands are attributed.

All the complexes show a strong absorption band in the 1500 cm^{-1} region. This band is attributed to the stretching vibration of C–N bond and indicates a considerable double bond character.

The position of the band is very slightly affected by the nature of the metal atom. As a rule, a slight shifting is observed toward lower frequencies from arsenic to bismuth complexes. This is justified by the fact that the charge transfer from the ligand to the metal atom ($R_2dtc \rightarrow M$) decreases from arsenic to bismuth according to their electron accepting ability.

TABLE II. Relevant I.r. Frequencies (cm^{-1}) of the Iodobis(dialkyldithiocarbamate) Complexes of Arsenic, Antimony and Bismuth with Their Assignments (KBr disks).[a]

Compound	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	Compound	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$
$IAs(Et_2dtc)_2$	1525vs, sh 1512vs (1515)[b]	996m 985m, sh 848s	$IBi(Bz_2dtc)_2$	1475vs	1002m 987m 880w
$ISb(Et_2dtc)_2$	1510vs, sh 1502vs (1505)	996m 987m 842s	$IAs(Pyrrdtc)_2$	1515vs, sh 1505vs (1510)	940s 824w
$IBi(Et_2dtc)_2$	1500vs 1486vs (1490)	984m 841s	$ISb(Pyrrdtc)_2$	1500vs, sh 1493vs (1495)	943s 824w
$IAs(i\text{-}Bu_2dtc)_2$	1517vs 1497vs (1505)	981w 885w 855w	$IBi(Pyrrdtc)_2$	1480vs	938s 827w
$ISb(i\text{-}Bu_2dtc)_2$	1500vs, sh 1495vs (1495)	974m 882w 858w	$IAs(Pipdtc)_2$	1530vs 1520vs (1525)	998s 886s
$IBi(i\text{-}Bu_2dtc)_2$	1485vs	970m 880w 857w	$ISb(Pipdtc)_2$	1520vs, sh 1504vs (1515)	1001vs 886s
$IAs(Bz_2dtc)_2$	1475vs	999m 880w	$IBi(Pipdtc)_2$	1492vs	1000vs 883s
$ISb(Bz_2dtc)_2$	1482vs	998m 985m 875w			

[a] vs = very strong, m = medium, sh = shoulder, w = weak, s = strong. [b] Values in parentheses refer to the center of the bands.

The stretching frequency of the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond is also affected by the electron releasing ability of the amine group following the sequence:

$$Bz_2N- < i\text{-}Bu_2N- \lesssim Pyrr \lesssim Et_2N- < Pip$$

This sequence is in accord with the increased basicity of the amine used, the only exception being the pyrrolidyl derivatives. The basicity of the amines is partly a measure of the inductive effect of their alkyl groups;[17] thus it follows that the effect of alkyl groups on the electronic structure of the dithiocarbamate complexes is inductive in accordance with the views of Cotton *et al.*[18] This is, however, contrary to the suggestions of Coucouvanis[19] and Selbin *et al.*[20] who support the idea that the effect of alkyl groups on the electronic structure of dithiocarbamate complexes is mainly a resonance effect.

The stretching frequencies of $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond of the iodobis(dialkyldithiocarbamate) complexes are higher than those of the corresponding tris(dialkyldithiocarbamate) complexes.[13] This is possibly due either to the different stereochemical structure of the complexes, or to the –I inductive effect of iodine resulting in an increase in the bond order of the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond. Based on the different polarity of the metal–iodine bonds, As–I<Sb–I<Bi–I, it would be expected that the introduction of an iodine atom would cause a greater shift of the band toward higher frequencies for the complexes of bismuth than for those of antimony and arsenic. The observed shifts do not follow the expected sequence, but, on the contrary, they decrease from the arsenic to bismuth compounds. This could be the result of the more pronounced π-back donation ($M_{(n\pi)} \rightarrow L_{(d\pi)}$ or $L_{(\pi^*)}$) in bismuth compounds compared to those of antimony and arsenic and is expected to be more favorable in iodobis(dialkyldithiocarbamate) complexes than in the tris(dialkyldithiocarbamate) complexes.

This explanation is supported by the fact that the dithiocarbamate ligands can act as π-electron acceptors because they have two sulfur atoms with vacant 3*d* orbitals and π^* molecular orbitals. The ability of dithiocarbamate ligands to act as π-acceptors is supported by the possible existence of π-conjugation.[21]

Another factor supporting the intensified appearence of π-back donation in the iodobis(dialkyldithiocarbamate) as compared to the tris(dialkyldithiocarbamate) complexes is based on the fact that the shifting of ν(C$\overset{\cdots}{-}$N) becomes greater as the electron releasing ability of the dialkylamino group increases. As the electron releasing ability of amine group increases, the electron density on the sulfur atoms also increases and consequently the dithiocarbamate ligands become weaker π-acceptors.

The bands which are attributed to the stretching vibration of the single bond between the nitrogen atom and the carbon atom of the alkyl groups are found in the 1200–1300 cm^{-1} region of the spectra. These are strong bands with several peaks. The number and the shapes of the peaks depend on the nature of dialkylamino groups. The stretching frequency of the bands increases as the double bond character of C$\overset{\cdots}{-}$N bond increases.

The exact assignment of the bands in the 800–1200 cm^{-1} region is considerably difficult because most of them are due to the conjugation of the stretching frequencies of the various bonds of the molecule. Certain bands found in the 1150, 940–1000 and 850–900 cm^{-1} regions may be attributed to the stretching vibration of C$\overset{\cdots}{-}$S bonds (Table II).

Though it should be expected, a direct relationship between the ν(C$\overset{\cdots}{-}$N) and ν(C$\overset{\cdots}{-}$S) frequencies[20] is not observed for these complexes. This is because the bands which are attributed to the stretching vibration of C$\overset{\cdots}{-}$S bonds are due only partly to the vibration of the bond.

The assignment of the above bands to the stretching vibration of C$\overset{\cdots}{-}$S bonds is also confirmed by comparing the spectra of the dialkyldithiocarbamates to those of the corresponding dialkyldiselenocarbamate complexes.[22,23] In the latter, the stretching vibration of the C$\overset{\cdots}{-}$Se bond appears at lower frequencies as is expected, because of the difference between the mass of selenium and that of sulfur.

The observed splitting of the band around the 1500 cm^{-1} region for some of the complexes, especially those of arsenic, proves the existence of nonequivalent dithiocarbamate ligands. Similar splittings have been observed by other researchers[24,25] and were applied for the distinction between mono- and bidentate dithiocarbamate ligands.

^{1}H N.m.r. Spectra

The signals of the ^{1}H n.m.r. spectra of the compounds are reported in Table III. They are sharp without being split and indicate the noncoexistence of mono- and bidentate dithiocarbamate ligands. This fact, however, does not imply directly that the two dithiocarbamate ligands are bonded equivalently, since the protons are at considerable distance from the metal–sulfur bonds.[26]

The signals of the methylene protons of the studied compounds are shifted toward higher frequencies (2–13 Hz) as compared to the signals of the methylene protons of the corresponding tris(dialkyldithiocarbamate) complexes.[13] This is unexpected because the electron density of the methylene protons of the studied compounds is lower than that of the methylene protons of the corresponding tris(dialkyldithiocarbamate) complexes. This is a result of the greater charge transfer from the ligand to the metal atom in the iodo-derivatives than in the trisdithiocarbamates as was ascertained from the study of their i.r. spectra. The observed shielding of the methylene protons when compared to the corresponding protons of the trisdithiocarbamates can possibly be attributed to the different location of these protons in the shielding cone of C$\overset{\cdots}{-}$N bond.[27]

The other protons which are more distant from the nitrogen atom undergo deshielding in comparison to the protons of the corresponding trisdithiocarbamates. This is a result of the –I inductive effect of the iodine

TABLE III. ^{1}H N.m.r. Spectra of Iodobis(dialkyldithiocarbamate) Complexes of Arsenic, Antimony and Bismuth.[a]

Amine Group	Protons	Arsenic Compounds			Antimony Compounds			Bismuth Compounds		
		τ(CDCl$_3$)	τ(C$_6$H$_6$)	$\Delta\tau$[b]	τ(CDCl$_3$)	τ(C$_6$H$_6$)	$\Delta\tau$	τ(CDCl$_3$)	τ(C$_6$H$_6$)	$\Delta\tau$
$-N(CH_2CH_3)_2$	$-CH_2-$	6.16q[c]	6.91q	0.75	6.16q	6.84q	0.68	6.22q	6.79q	0.58
	$-CH_3$	8.65t	9.32t	0.67	8.66t	9.27t	0.61	8.62t	9.16t	0.54
$-N[CH_2CH(CH_3)_2]_2$	$-CH_2-$	6.32d	6.67d	0.35	6.33d	6.66d	0.33	6.40d	6.60d	0.20
	$-CH=$	7.66m	8.00m	0.34	7.63m	7.95m	0.32	7.52m	7.73m	0.21
	$-CH_3$	9.02d	9.36d	0.34	9.02d	9.34d	0.32	9.03d	9.26d	0.23
$-N(CH_2C_6H_5)_2$	$-CH_2-$	4.98s	5.16s[d]	0.18	4.96s	5.24s[d]	0.28	5.10s	5.25s[d]	0.15
	$-C_6H_5$	2.66s	2.89s	0.23	2.58s	2.89s	0.31	2.68s	2.87s	0.19

[a] τ values in p.p.m. relative to TMS as internal standard. [b] $\Delta\tau = \tau(C_6H_6)-\tau(CDCl_3)$. [c] q = quartet, t = triplet, d = doublet, m = multiplet, s = singlet. [d] In C_6D_6 solution.

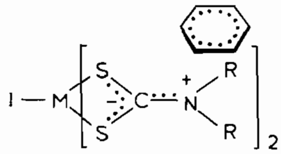
atom and the position of these protons in the deshielding cone of the C$\overset{\cdots}{-}$N bond.

The influence of the magnetic anisotropy of the C$\overset{\cdots}{-}$N bond on the chemical shift of the methylene protons of the studied compounds becomes greater as the bond order of the C$\overset{\cdots}{-}$N bond increases. This becomes obvious after observing that, as the electron releasing ability of amine group increases, the shifting of the signals of the methylene protons to lower frequencies is smaller when compared to the signals of the corresponding protons of the free amines. Thus, the observed decrease in the difference of the chemical shift of methylene protons between the iodobis(dialkyldithiocarbamate) and their corresponding tris(dialkyldithiocarbamate) complexes as the difference in the stretching frequency of their C$\overset{\cdots}{-}$N bonds increases is also justified.

The shielding of the methylene protons of the iodobis(dialkyldithiocarbamate) complexes compared to the tris(dialkyldithiocarbamate) complexes depends on the nature of the metal and follows the sequence $\mathrm{Bi} \gtrsim \mathrm{As} > \mathrm{Sb}$. This can be attributed to the more intense π-back donation in bismuth compounds as compared to those of antimony and arsenic, as shown by the study of their i.r. spectra.

The ^1H signals of the compounds in benzene solution undergo a shift toward higher frequencies as compared to inert solvents (Table III). This shift is attributed to the formation of weak collision complexes between benzene (solvent) and the dissolved compounds (solutes).[28]

These complexes could be represented as follows:



The signals of the various protons in each dithiocarbamate ligand undergo a different shift in benzene solution as compared to inert solvents. This is because these protons are located in different positions within the shielding cone of benzene molecule.

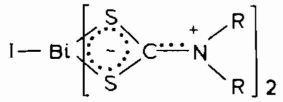
It is also observed that as the electron density of the nitrogen atom of the dithiocarbamate ligands is decreased, the shifting of the resonance signals of their protons in benzene solution as compared to inert solvent is increased. Thus, the signals of the protons of the iodobis(dialkyldithiocarbamate) complexes undergo a greater shifting than the corresponding protons of trisdithiocarbamates, because of the increased positive charge on the nitrogen atom. This is in agreement with the general rule that protons situated in an area of high electron density tend toward deshielding in benzene solution as compared to inert solvent, while those protons found in areas of low electron density undergo shielding.[29] In some cases, however, the stereochemistry of the complexes should be taken into consideration.

In the case of diethyldithiocarbamatodiethylammonium, which is an ionic compound, its ^1H n.m.r. signals undergo very small shifts in benzene solution as compared to inert solvent.[30] This shows that the effect of benzene on the ^1H n.m.r. signals of dialkyldithiocarbamate complexes could be used to ascertain the type of coordination of the dithiocarbamate ligands.

Electronic Spectra

Table IV gives the absorption maxima and the molecular extinction coefficients of the electronic spectra of the iodobis(dialkyldithiocarbamate) complexes. All the complexes in chloroform solution show three absorption bands (band I, II and III). These bands are attributed to the chromophore group NCS_2.[31]

The most intense, band I, is due to an intraligand $\pi \rightarrow \pi^*$ transition of the N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$S group.[32,33] The position of band I is slightly affected by the nature of the central atom. Usually, the frequencies follow the order $\mathrm{As} \gtrsim \mathrm{Bi} \gtrsim \mathrm{Sb}$. But on the basis of the electronegativities of the elements the sequence $\mathrm{As} > \mathrm{Sb} > \mathrm{Bi}$ is expected, and is the trend observed in the case of the tris(dialkyldithiocarbamate) complexes. This discrepancy shows that the π-back donation is more pronounced in the iodobis(dialkyldithiocarbamate) complexes, especially in those of bismuth, than in the corresponding tris(dialkyldithiocarbamate) complexes. The result is an increase in the bond order of the chelate rings, which justifies the observed sequence:



Another indication of the more pronounced π-back donation in the iodobis(dialkyldithiocarbamate) complexes is the fact that the position of band I of the iodocompounds is shifted toward higher frequencies relative to the corresponding tris(dialkyldithiocarbamate) complexes. This is especially true in the case of the bismuth compounds.

The position of band I is also affected by the electron releasing ability of the amine group, and as this ability increases a shift toward higher frequencies is observed. Consequently, as in the case of tris(dialkyldithiocarbamate) complexes[13], the following is the spectrochemical series of the dithiocarbamate ligands used:

$$\mathrm{Pyrrdtc} > \mathrm{Et_2dtc} > \mathrm{Pipdtc} \gtrsim \mathrm{i\text{-}Bu_2dtc} > \mathrm{Bz_2dtc}$$

A similar order was suggested by Eley *et al.*[34] for the dithiocarbamate ligands. Their conclusions are based on the results of magnetic moment data of a

TABLE IV. Electronic Spectra of Iodobis(dialkyldithiocarbamate) Complexes of Arsenic, Antimony and Bismuth.[a]

Compound	Band I			Band II		Band III	
	ν_{max}(kK)	logε_{mol}	$\delta-$(kK)[b]	ν_{max}(kK)	logε_{mol}	ν_{max}(kK)	logε_{mol}
IAs(Et$_2$dtc)$_2$	39.4	4.65	4.4	31.8sh[c]	4.18	27.9sh	3.80
ISb(Et$_2$dtc)$_2$	39.1	4.63	4.4	31.8sh	4.04	26.6sh	3.48
IBi(Et$_2$dtc)$_2$	39.2	4.70	3.4	31.4sh	3.90	26.0	3.88
IAs(i-Bu$_2$dtc)$_2$	38.8	4.66	4.6	31.8sh	4.23	27.7sh	3.79
ISb(i-Bu$_2$dtc)$_2$	38.3	4.66	4.2	31.8sh	4.11	26.6sh	3.48
IBi(i-Bu$_2$dtc)$_2$	38.8	4.70	3.6	31.2sh	3.95	25.9	3.94
IAs(Bz$_2$dtc)$_2$	38.6	4.72	4.2	32.0sh	4.23	27.4sh	3.62
ISb(Bz$_2$dtc)$_2$	38.2	4.67	4.1	32.0sh	4.15	26.3sh	3.49
IBi(Bz$_2$dtc)$_2$	38.5	4.74	3.4	30.8sh	4.00	25.9	3.93
IAs(Pyrrdtc)$_2$	39.9	4.59	5.1	32.2sh	4.08	28.0sh	3.81
ISb(Pyrrdtc)$_2$	39.6	4.63	5.0	32.0sh	4.04	26.8sh	3.49
IBi(Pyrrdtc)$_2$	39.5	4.69	3.7	31.4sh	3.90	26.5	3.86
IAs(Pipdtc)$_2$	39.1	4.59	4.9	31.8sh	4.11	27.9sh	3.79
ISb(Pipdtc)$_2$	38.7	4.63	4.3	31.8sh	4.08	26.7sh	3.51
IBi(Pipdtc)$_2$	38.8	4.72	3.4	31.0sh	3.95	26.0	3.93

[a] In CHCl$_3$ solution. [b] Only $\delta-$ values are given because $\delta+$ could not be reliably determined. $\Delta\nu = \delta+ + \delta-$ where $\Delta\nu$ is the half band width. [c] sh = Shoulder.

large number of tris(dialkyldithiocarbamate) complexes of iron. This is also the sequence of the increasing ligand field strength of the ligands used.

The molecular extinction coefficient of band I is slightly affected by the nature of the dithiocarbamate ligand and the nature of the metal atom. Yet, it decreases considerably from the tris(dialkyldithiocarbamate) to the iodobis(dialkyldithiocarbamate) complexes.

As a rule, it is observed that the molecular extinction coefficient of band I decreases as the charge transfer from the ligand to metal atom increases. This is possibly due to the decrease in the difference of polarity between ground and excited states.

Though the absorption maximum is slightly affected by the nature of the metal atom, yet one can observe important differences in the values of $\delta-$ of band I. Thus, $\delta-$ decreases considerably from the arsenic to the bismuth compounds as well as from the iodobis (dialkyldithiocarbamate) to the tris(dialkyldithiocarbamate) complexes.

This can be explained if we assume that an almost parallel shift takes place for both π and π^* molecular orbitals of NCS$_2$ group of the ligands after their coordination, which decreases as the charge transfer dtc→M decreases according to the aforementioned sequences.[35]

Band II, which appears as a shoulder, is also attributed to a $\pi\rightarrow\pi^*$ transition of the $S\overset{\cdots}{-}C\overset{\cdots}{-}S$ group[36] and is associated with the inequivalence of the $C\overset{\cdots}{-}S$ bonds of the ligands. Band II of the iodocompounds is less characteristic than that of the corresponding trisdithiocarbamates, and tends to disappear in the antimony and bismuth compounds. This may be attributed to the fact that in these cases the dithiocarbamate ligands are coordinated to the metal more equivalently, which is in agreement with their i.r. spectra.

Band III also appears as a shoulder in the compounds of arsenic and antimony. In the spectra of the bismuth compounds, however, band III shows a characteristic maximum. This band was assigned by several authors[37,38] to an $n\rightarrow\pi^*$ electronic transition located on the sulfur atom, while others[30] assigned it to a charge transfer from the ligand to the metal. The frequency of band III decreases, as a rule, from the arsenic to bismuth compounds and from the tris(dialkyldithiocarbamate) to the iodobis(dialkyldithiocarbamate) complexes. Also, the frequency of band III is slightly increased as the electron releasing ability of amine group increases. These observations can be justified if we ascribe the band to an $\eta\rightarrow\pi^*$ transition located on the sulfur atom, because it is known that an increase in the electron density of a chromophore group results in a blue shift of the $\eta\rightarrow\pi^*$ band.[39]

The more pronounced π-back donation in iodobis (dialkyldithiocarbamate) complexes justifies the lower frequency of band III in these relative to the tris(dialkyldithiocarbamate) complexes.

In the case of the bismuth compounds, band III is possibly overlapped by another band as a result of an electron transition within the metal atom. A similar explanation is also suggested by other authors for analogous bismuth compounds.[32,40]

Mass Spectra

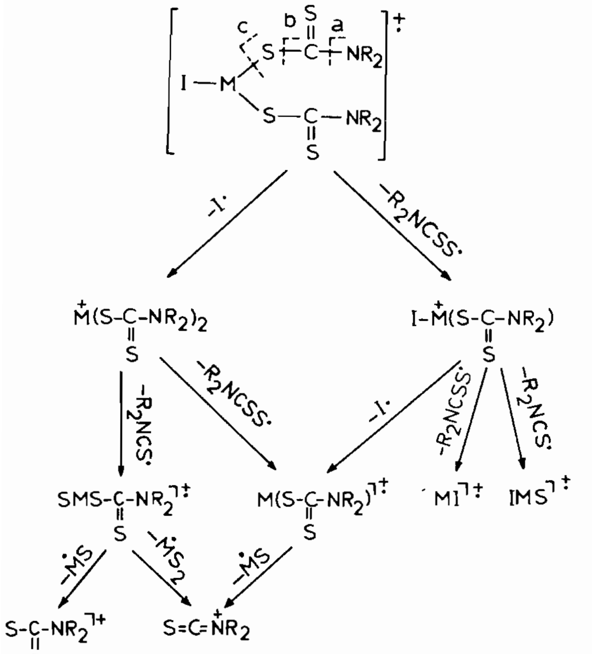
Table V gives the most relevant mass spectral (m.s.) peaks of some of the more representative complexes under study. Figure 1 shows a typical mass spectrum.

In these spectra, as in the case of tris(dialkyldithiocarbamate) complexes of arsenic, antimony and bismuth[15] the molecular ion was not found. This can be attributed either to a pyrolytic decomposition because of the relatively high temperature (170–250°C) used, or to the fragmentation of the molecular ion in the ionization chamber.

The peaks corresponding to higher m/e values can be regarded as direct fragments of the molecular ions and are the ones corresponding to the formulae,

$$\overset{+}{M}[SC(S)NR_2]_2 \quad \text{and} \quad I\overset{+}{M}[SC(S)NR_2]$$
$$\text{(I)} \qquad\qquad \text{(II)}$$

The fragments corresponding to lower m/e values may be regarded as daughter fragments of ions I and II. A possible fragmentation mechanism of the molecular ion is represented by Scheme 1:



Scheme 1

The base peak in the m.s. of the compounds varies according to the temperature of the ionization chamber and the type of amine group of the dithiocarbamate ligand. The base peak corresponds, usually, either to the $[R_2NCS]^+$ or to the $[CS_2]^{\ddagger}$ ion. Therefore, it can be assumed that the aforementioned ions result, partially, from the pyrolytic decomposition of the molecule. Also, in the m.s. of the compounds peaks which correspond to the fragments of the dithiocarbamate ligands are found (Scheme 1, ions a, b, c).

Metastable peaks are not found, except in the case of the iodobi(pyrrolidyldithiocarbamato)arsine. For this complex a metastable peak at m* = 51.3 was

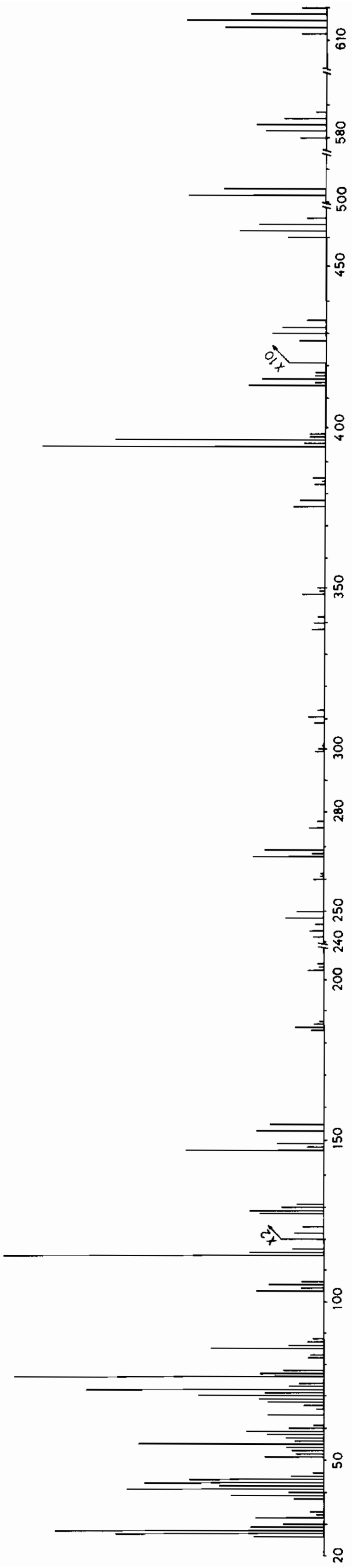


Figure 1. Mass spectrum of iodobi(pyrrolidyldithiocarbamato)stibine.

TABLE V. Mass Spectra of Some Iodobis(dialkyldithiocarbamate) Complexes of Arsenic, Antimony and Bismuth.

$IAs(Pyrrdtc)_2$		$ISb(Pyrrdtc)_2$		$IBi(Pyrrdtc)_2$		$IAs(i\text{-}Bu_2dtc)_2$		$IBi(Et_2dtc)_2$	
m/e	R.I.[a]	m/e	R.I.	m/e	R.I.	m/e	R.I.	m/e	R.I.
44	16.3	44	41.3	44	90.9	41	100.0	44	51.4
59	16.3	59	24.1	59	16.0	44	26.1	55	28.5
64	12.6	64	17.2	64	31.8	57	65.3	59	74.2
70	31.5	70	38.7	70	51.5	64	11.5	64	57.1
72	71.0	72	75.0	72	33.3	73	27.6	72	54.2
76	78.9	76	96.5	76	100.0	76	10.0	76	100.0
107	19.4	114	100.0	114	57.5	107	5.3	87	88.5
114	100.0	121	4.3	127	3.3	115	61.5	116	74.2
127	7.8	127	10.3	128	4.5	127	1.3	127	5.7
128	9.4	128	11.2	147	14.2	128	2.0	128	6.0
139	1.0	147	21.5	184	3.6	139	1.3	149	28.5
147	14.2	153	10.3	209	12.7	150	7.6	209	20.0
150	5.7	184	1.7	241	2.1	171	3.0	241	6.0
184	2.1	185	4.3	260	1.5	172	6.1	264	1.7
202	1.5	242	1.2	323	25.7	182	1.0	336	33.4
214	1.0	248	6.0	336	48.4	202	0.6	357	18.5
221	3.1	260	1.2	355	10.6	204	2.1	368	0.5
234	1.5	267	11.2	368	0.6	214	1.0	389	8.8
253	26.3	276	1.7	418	0.3	221	0.9	418	4.0
260	6.3	299	1.2	463	1.8	257	1.5	463	6.5
289	1.0	308	1.2	482	11.8	279	0.9	484	3.4
300	1.0	337	1.2	501	13.6	289	1.0	505	2.2
316	2.1	375	5.1			300	1.4		
321	2.3	382	1.2			311	2.8		
329	0.7	394	43.9			321	1.3		
335	1.5	413	12.0			376	0.4		
348	8.9	427	0.8			396	2.0		
367	3.1	459	1.2			406	0.8		
396	6.3	502	4.3			428	1.3		
404	0.1	580	0.8			451	0.1		
428	1.8	612	0.8			483	1.2		
456	0.5								

[a] R.I. = Relative Intensity.

observed, and corresponds to the following fragmentation:

$$\underset{m/e\ 253}{SAs[SC(S)N(CH_2)_4]^{+\cdot}} \xrightarrow[-139]{-A\dot{s}S_2} \underset{m/e\ 114}{[SCN(CH_2)_4]^{+}}$$

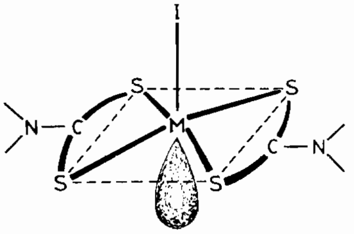
Finally, in the m.s. of the studied compounds peaks are found which can be attributed to polynuclear metal ions or their sulfides of the general formula M_nS_m (where M = As, Sb or Bi; n = 1, 2, 3, 4; m = 0–5). These ions can be regarded as resulting from the pyrolytic decomposition of the complexes, during which condensation reactions take place forming polynuclear compounds. These undergo further fragmentation to produce the polynuclear ions.

Molecular Weights

Molecular weight determinations of all the compounds studied, except those of bismuth, show that they are monomers in $CHCl_3$ solution in the concentration range 10^{-3}–$10^{-4}m$. The bismuth complexes tend to be dimerized. This tendency of bismuth for dimerization decreases as the electron releasing ability of amine group increases. Because of its ability to cause more pronounced π-back donation, dimerization in this case is associated with the lower electron density on the bismuth atom. As a result weak forces exist between the bismuth atom of one molecule and an iodine atom of another.

Conclusions

Fifteen new iodobis(dialkyldithiocarbamate) complexes of three of the Group VA elements, arsenic, antimony and bismuth, were prepared and characterized. The results of spectroscopic studies indicate that the dithiocarbamate groups function as bidentate ligands, and thus, the central atom in these complexes must have a coordination number of five. Therefore, their structure can be either a square pyramid or a trigonal bipyramid. But, if the fact that π-back donation is stronger in these compounds than in the corresponding trisdithiocarbamates is considered, then the square pyramid seems the most likely structural choice:



That this is the case is further supported by the work of other authors which demonstrates that π-back donation is favored by the square pyramidal rather than by the trigonal bipyramidal structure.[41] Moreover, the square pyramid structure is in accord with the X-ray data obtained for the bromo- and phenylbis(diethyldithiocarbamato) arsines.[11,12] Thus, the square pyramid appears to be the more stable structure when π-back donation is involved, even though it is known and generally accepted that five-coordinate complexes of the non-transition metals adopt the trigonal bipyramidal structure.[21]

The hybridization of the central atom of each complex is probably of the sp^3d^2 type. Hence, five hybrid orbitals are used for the formation of the coordinate bonds and one is occupied by a lone pair of electrons.

Experimental

Physical Measurements

Infrared spectra were recorded on a Perkin–Elmer 257 spectrophotometer, using KBr pellets and in most cases chloroform solutions, in the range 4000–650 cm^{-1}. No significant differences between solid state and solution spectra were noted.

^{1}H n.m.r. spectra were recorded on a Variam A 60A (60 Mc/s) instrument in $CDCl_3$ and C_6H_6 solutions using TMS as internal standard.

Electronic spectra were obtained with a Zeiss PMQ II spectrophotometer with freshly prepared $CHCl_3$ solutions at about 30°C. Mass spectra were performed on a RMU-6L Hitachi Perkin–Elmer single-focusing mass spectrometer. The operating conditions were 70 eV electron energy using the direct probe insertion of thc samples at 170–250°C. The ion source used was a T-2*p* model. Molecular weights were determined using a Perkin–Elmer molecular weight apparatus Model 115 in a concentration range 3×10^{-3}–$6\times10^{-4}m$ in $CHCl_3$ solution.

Preparation of the Complexes

The tris(dialkyldithiocarbamate) complexes of arsenic, antimony and bismuth were prepared according to the published method.[13]

The iodobis(dialkyldithiocarbamate) complexes were prepared as follows.

Iodobis(diethyldithiocarbamato)arsine, (I), $IAs[SC(S)N(C_2H_5)_2]_2$

To a solution of tris(diethyldithiocarbamato)arsine (5.0 mmol) in 30 ml of benzene, a solution of iodine (2.5 mmol) in 23 ml CCl_4 was added dropwise, while stirring constantly. After the addition of the iodine solution, the mixture was stirred at room temperature for 24 hours, whereupon a yellow precipitate appeared. The reaction mixture was filtered, the precipitate washed with methanol and then dried under vacuum. The precipitate was recrystallized from a mixture of chloroform and methanol or from benzene. Compound (I) is soluble in chloroform, methylene chloride, pyridine and dimethylformamide, but is insoluble in carbon tetrachloride, benzene, petroleum ether, water, methanol and ethanol.

Iodobis(diethyldithiocarbamato)stibine (II), $ISb[SC(S)N(C_2H_5)_2]_2$

Compound II was prepared by a method similar to that described above. Thus, 10.0 mmol of tris(diethyldithiocarbamato)stibine dissolved in a mixture of 70 ml CCl_4 and 15 ml $CHCl_3$, and 5.0 mmol of iodine dissolved in 46 ml CCl_4 were employed. The mixture was stirred for 4 hours. Recrystallization was carried out from a mixture of $CHCl_3$ and methanol or from benzene. The solubility of compound (II) is similar to that of compound (I).

Iodobis(diethyldithiocarbamato)bismuthine, (III), $IBi[SC(S)N(C_2H_5)_2]_2$

A method similar to that described above was followed. 5.5 mmol of tris(diethyldithiocarbamato)bismuthine dissolved in 80 ml of a mixture of equal volumes of CCl_4 and $CHCl_3$ was treated with 2.75 mmol of iodine dissolved in 25 ml CCl_4. The mixture was stirred for 4 hours and was then filtered and the precipitate washed with ethanol. The filtrate was concentrated to a small volume (≅40 ml) and upon addition of methanol more of compound (III) was precipitated. Recrystallization was carried out from a mixture of $CHCl_3$ and ethanol or methanol. The solubility of this compound is similar to that of compound (I).

Iodobis(diisobutyldithiocarbamato)arsine, (IV), IAs$[SC(S)N(i\text{-}C_4H_9)_2]_2$, *Iodobis(diisobutyldithiocarbamato)stibine, (V), ISb*$[SC(S)N(i\text{-}C_4H_9)_2]_2$ *and Iodobis(diisobutyldithiocarbamato)bismuthine, (VI), IBi*$[SC(S)N(i\text{-}C_4H_9)_2]_2$

These compounds were prepared by a method similar to that described for the preparation of compound (I). 5.0 mmol of the corresponding tris(diisobutyldithiocarbamate) complex dissolved in 50 ml CCl_4 and 2.5 mmol of iodine dissolved in 23 ml CCl_4 were employed. The mixture was stirred for 4 hours. After the mixture was filtered, the filtrate was evaporated to about 20 ml and then methanol or ethanol was added to yield the corresponding iodobis(diisobutyldithiocarbamate) complex as a precipitate. Recrystallization of compounds (IV), (V) and (VI) was carried out from a mixture of benzene and methanol or carbon tetrachloride and methanol. These compounds are soluble in chloroform, methylene chloride, carbon tetrachloride, benzene, pyridine and acetone, but are insoluble in ethanol, methanol, petroleum ether and water.

Iodobis(dibenzyldithiocarbamato)arsine, (VII), IAs$[SC(S)N(CH_2C_6H_5)_2]_2$

2.5 mmol of tris(dibenzyldithiocarbamato)arsine dissolved in 25 ml $CHCl_3$ was treated with 1.25 mmol of iodine dissolved in 12 ml $CHCl_3$ according to the method already described for the preparation of compound (I). After the addition of the iodine solution, 50 ml of methanol were added and the mixture was stirred for 24 hours at room temperature. The resulting precipitate was isotated by filtration, washed with methanol and dried under vacuum. Purification of the complex was carried out by dissolving the crude product in a small amount of benzene at room temperature, filtering the solution and diluting the filtrate with methanol until no precipitation of the complex was observed. When reprecipitating the complex, a viscous oil was obtained which was solidified on drying under vacuum. The solubility of compound (VII) is similar to that of compound (IV).

Iodobis(dibenzyldithiocarbamato)stibine, (VIII), ISb$[SC(S)N(CH_2C_6H_5)_2]_2$

A method similar to that described for the preparation of compound (I) was followed. 5.0 mmol of tris(dibenzyldithiocarbamato)stibine dissolved in 100 ml CCl_4 and 2.5 mmol of iodine dissolved in 23 ml CCl_4 were employed. The reaction was complete in 6 hours. After the solution was filtered, the filtrate was concentrated to about 50 ml and methanol or petroleum ether was added to the solution to yield the complex as a viscous oil, which was solidified under vacuum. Purification was carried out as in the case of compound (VII). Its solubility is similar to that of compound (IV).

Iodobis(dibenzyldithiocarbamato)bismuthine, (IX), IBi$[SC(S)N(CH_2C_6H_5)_2]_2$

Compound (IX) was prepared by a procedure analogous to that described for the preparation of compound (VIII). Recrystallization was carried out from a mixture of benzene and petroleum ether or benzene and methanol. Its solubility is analogous to that of compound (IV).

Iodobi(pyrrolidyldithiocarbamato)arsine, (X), IAs$[SC(S)NC_4H_8]_2$, *Iodobi(pyrrolidyldithiocarbamato)stibine, (XI), ISb*$[SC(S)NC_4H_8]_2$ *and Iodobi(pyrrolidyldithiocarbamato)bismuthine, (XII), IBi*$[SC(S)NC_4H_8]_2$

These compounds were prepared by a procedure similar to that described above. 5.0 mmol of the corresponding tri(pyrrolidyldithiocarbamate) complex dissolved in 100 ml $CHCl_3$ and 2.5 mmol of iodine in 25 ml $CHCl_3$ were employed. The reaction was complete in 6 hours for compound (X) and in 4 hours for the other compounds. In the case of compound (X), a deep red precipitate was formed during the stirring of the solution. These compounds were recrystallized from a mixture of dimethylformamide and ethanol or from chloroform or methylene chloride. The above compounds are soluble in dimethylformamide and dimethylsulfoxide, slightly soluble in chloroform and methylene chloride and insoluble in the most common organic solvents and water.

After the isolation of compounds (X), (XI) and (XII) from the corresponding solutions of their preparation reactions by filtration, the filtrate was concentrated up to ~30 ml and methanol was added to yield a white crystalline precipitate. This precipitate was recrystallized from a mixture of chloroform and methanol or from acetone, and was identified as dipyrrolidylthiuramdisulfide by its elemental analysis and i.r. spectrum. *Anal.* Calcd for $[(CH_2)_4NCSS]_2$ C, 41.06; H, 5.51; N, 9.58%. Found: C, 40.98; H, 5.53; N, 9.52%.

Iodobi(piperidyldithiocarbamato)arsine, (XIII), IAs$[SC(S)NC_5H_{10}]_2$, *Iodobi(piperidyldithiocarbamato)stibine, (XIV), ISb*$[SC(S)NC_5H_{10}]_2$ *and Iodobi(piperidyldithiocarbamato)bismuthine, (XV), IBi*$[SC(S)NC_5H_{10}]_2$

A procedure similar to that described above was followed. 5.0 mmol of the corresponding tri(piperidyldithiocarbamate) complex dissolved in 80 ml $CHCl_3$ and 2.5 mmol of iodine dissolved in 25 ml $CHCl_3$ were employed. The reaction was complete in 4 hours. After the mixtures were filtered, the filtrates were evaporated to about 40 ml, and then methanol was added to yield more of the corresponding compounds. The new filtrate was concentrated to a small volume and a quantity of methanol was added After allowing this solution to stand in the atmosphere for several days, the dipiperidylthiuramdisulfide was obtained.

The dipiperidylthiuramdisulfide was recrystallized from a mixture of benzene and methanol and was identified from its elemental analysis, i.r. spectrum and melting point, 130–131°C.[43] Compound (XIII) was recrystallized from chloroform or methylene chloride. Compounds (XIV) and (XV) were recrystallized from dimethylformamide or chloroform or methylene chloride. The solubility of the above compounds is similar to that of compound (X).

References

1 H.J.A. Blaauw, R.J.F. Nivard and G.J.M. van der Kerk, *J. Organometal. Chem., 2,* 236 (1964).

2 P.T. Beurskens, H.J.A. Blaauw, J.A. Cras and J.J. Steggerda, *Inorg. Chem., 7,* 805 (1968).

3 P.T. Beurskens, J.A. Cras and J.J. Steggerda, *Inorg. Chem., 7,* 810 (1968).

4 H.C. Brinkhoff, J.A. Cras, J.J. Steggerda and J. Willemse, *Recl. Trav. Chim. Pays-Bas, 88,* 633 (1969).

5 P.T. Beurskens, J.A. Cras and J.G. van der Linden, *Inorg. Chem., 9,* 475 (1970).

6 H.C. Brinkhoff, *Recl. Trav. Chim. Pays-Bas, 90,* 377 (1971).

7 Y. Nigo, I. Masuda and K. Shinra, *Chem. Commun.,* 476 (1970).

8 J. Willemse and J.J. Steggerda, *Chem. Commun.,* 1123 (1969).

9 R.M. Goldin, C.M. Harris, K.J. Jessop and W.C. Tennant, *Aust. J. Chem., 25,* 2567 (1972).

10 F. Bonati and G. Minghetti, *Chim. Ind. (Milan), 52,* 1204 (1970).

11 R. Bally, *C.R. Acad. Sc. Paris, t. 271,* 1436 (1970).

12 G.E. Manoussakis, C.A. Tsipis and C.C. Hadjikostas, *Canad. J. Chem., 53,* 1530 (1975).

13 a) G.E. Manoussakis and C.A. Tsipis, *J. Inorg. Nucl. Chem., 35,* 743 (1973); b) C.A. Tsipis, Unpublished results.

14 H.P. Koch, *J. Chem. Soc.,* 401 (1949).

15 G.E. Manoussakis, E.D. Mikromastoras and C.A. Tsipis, *Z. Anorg. Allg. Chem., 403,* 87 (1974).

16 M. Colapietro, A. Domenicano, L. Scaramuzza and A. Vaciago, *Chem. Commun.,* 302 (1968).

17 H.K. Hall, *J. Am. Chem. Soc., 79,* 5441 (1957).

18 F.A. Cotton and J.A. McCleverty, *Inorg. Chem., 3,* 1398 (1964).

19 D. Coucouvanis and J.P. Fackler, *Inorg. Chem., 6,* 2047 (1967).

20 G. Vigee and J. Selbin, *J. Inorg. Nucl. Chem., 31,* 3187 (1969).

21 B.F. Hoskins and F.D. Whillans, *Coord. Chem. Rev., 9,* 365 (1973).

22 G.E. Manoussakis, C.A. Tsipis and A.G. Christophides, *Inorg. Chem., 12,* 3015 (1973).

23 G.E. Manoussakis, C.A. Tsipis and A.G. Christophides, *Z. Anorg. Allg. Chem.,* in press.

24 C. O'Connor, J.D. Gilbert and G. Wilkinson, *J. Chem. Soc. A,* 84 (1969).

25 G.St. Nikolov, N. Jordanov and K. Daskalova, *Inorg. Nucl. Chem. Lett., 6,* 723 (1970).

26 J.P. Bibler and D.G. Karraker, *Inorg. Chem., 7,* 982 (1968).

27 G.J. Karabatsos, G.C. Sonnichsen, N. Hsi and D.J. Fenoglio, *J. Am. Chem. Soc., 89,* 5067 (1967).

28 G.E. Manoussakis and C.A. Tsipis, *Z. Anorg. Allg. Chem., 398,* 88 (1973).

29 K.M. Baker and R.G. Wilson, *J. Chem. Soc. B,* 236 (1970).

30 D.C. Bradley and M.H. Gitlitz, *J. Chem. Soc. A,* 1152 (1969).

31 C.K. Jørgensen, "Inorganic Complexes", p. 138, Academic Press, London (1963).

32 C.K. Jørgensen, *J. Inorg. Nucl. Chem., 24,* 1571 (1962).

33 F. Takami, S. Wakahara and T. Maeda, *Tetrahedron Letters, 28,* 2645 (1971).

34 R.R. Elcy, R.R. Myers and N.V. Duffy, *Inorg. Chem., 11,* 1128 (1972).

35 G.St. Nikolov, N. Jordanov and I. Havezov, *J. Inorg. Nucl. Chem., 33,* 1059 (1971).

36 M.J. Janssen, *Recl. Trav. Chim. Pays-Bas, 79,* 1066 (1960).

37 M.J. Janssen, *Recl. Trav. Chim. Pays-Bas, 79,* 454 (1960).

38 M.L. Shankaranarayana and C.C. Patel, *Acta Chem. Scand., 19,* 1113 (1965).

39 R.S. Drago, "Physical Methods in Inorganic Chemistry", p. 253, Reinhold (1965).

40 V. Krishnan and R.A. Zingaro, *Inorg. Chem., 8,* 2337 (1969).

41 C. Furlani, *Coord. Chem. Rev., 3,* 141 (1968).

42 R. Bally, *Acta Cryst., 23,* 295 (1967).

43 G.D. Thorn and R.A. Ludwig, "The Dithiocarbamates and Related Compounds", Elsevier, Amsterdam (1962).