

COMPLEXES OF PHENYLDIHALOBISMUTHINES WITH 1,10-PHENANTHROLINE AND 2,2'-BIPYRIDINE

S. FALESCHINI, P. ZANELLA, L. DORETTI and G. FARAGLIA

Laboratorio di Chimica e Tecnologia dei Radioelementi—C.N.R.—Padova (Italy)

(Received May 5th, 1972)

SUMMARY

The molecular addition compounds of phenyldihalobismuthines with 1,10-phenanthroline and 2,2'-bipyridine have been isolated, and characterized by UV-visible, and IR spectrophotometry. The compounds have been obtained from non-aqueous media; they have empirical formulae of the type $C_6H_5BiX_2 \cdot L$ ($X = Cl, Br, I$; $L = Phen, Bipy$).

INTRODUCTION

The complexes of monophenylbismuthines have not been much studied. One of us (G.F.) prepared anionic complexes of $C_6H_5Bi^{III}$, containing the species $C_6H_5BiX_3^-$ ($X = Cl, Br, I$)¹. Monophenylbismuthines gave the adducts $C_6H_5BiX_2 \cdot 2Py$ ($X = Cl, Br$)² and $C_6H_5BiBr_2 \cdot Bipy$ ³ with neutral nitrogen ligands, and compounds of the type $C_6H_5Bi(S_2CNR_2)$ ⁴ with bidentate sulfur ligands.

This paper reports the preparation of the adducts of phenyldihalobismuthines with the neutral bidentate ligands 1,10-phenanthroline (Phen) and 2,2'-bipyridine (Bipy), and their characterization by UV-visible and infrared spectra;

EXPERIMENTAL

The materials used were as follows: commercial $(C_6H_5)_3Bi$ (Fluka) was purified by dissolving it in anhydrous ethyl ether, and removing the solvent under vacuum after filtration; $C_6H_5BiBr_2$ was prepared either from $BiBr_3$ and $(C_6H_5)_3Bi$ (molar ratio 2/1) in anhydrous ethyl ether⁵ or from $(C_6H_5)_2BiBr$ and bromine (molar ratio 1/1) in anhydrous chloroform, and crystallized from anhydrous benzene; $C_6H_5BiI_2$ from $(C_6H_5)_3Bi$ and iodine in ethyl ether^{5,6}, and used without further purification; $C_6H_5BiCl_2$ has not been isolated in the solid state owing to its ready decomposition and immediate hydrolysis in presence of traces of moisture. Solutions of phenyldichlorobismuthine in anhydrous acetone were obtained by reaction of $(C_6H_5)_3Bi$ and $BiCl_3$ (molar ratio 1/2), or alternatively, by adding a methanolic solution of anhydrous hydrochloric acid (concentration about 1 M, prepared from HCl gas) to $(C_6H_5)_3Bi$ dissolved in acetone (2 mmoles in 50 ml, molar ratio 2/1). $BiCl_3$ (C.Erba), dried over P_2O_5 and KOH, was dissolved in toluene/ether, and was isolated

as the toluene adduct by adding hexane⁷; toluene was removed by flushing with dry nitrogen followed by pumping under vacuum. BiBr₃ (Alpha-Inorganics), dried over P₂O₅, was recrystallized from anhydrous *p*-xylene/hexane⁷. Bipyridine (C.Erba) was sublimed *in vacuo* after drying over P₂O₅. Phenanthroline monohydrate (C.Erba) was heated under vacuum at about 70° for two hours (m.p. = 117–118°).

The solvents used in preparations and measurements were purified and dried by the usual methods⁸, and were stored under dry nitrogen. All operations involving bismuth halides and phenyldihalobismuthines were carried out in a dry-box filled with nitrogen and kept dry with Na/K alloy.

The complexes of the phenylbismuthines with both ligands were prepared as follows: to a solution of phenyldihalobismuthine (2 mmoles in about 20 ml of acetone) was added an anionic solution of the ligand (2 mmoles in about 15 ml). The adduct precipitated immediately, in a nearly quantitative yield, generally in a microcrystalline form. The solid was washed with acetone and dried *in vacuo* over P₂O₅.

TABLE 1

MELTING POINTS, ANALYSES, AND MOLAR CONDUCTIVITIES (OHM⁻¹·CM²·MOLE⁻¹) IN ANHYDROUS NITROMETHANE

Compounds	M.p. (°C)	Analysis found (calcd.) (%)				Λ (conc.: 3 × 10 ⁻⁴ M)
		C	H	N	Hal	
(I) C ₆ H ₅ BiCl ₂ ·Bipy	244–247	37.24 (37.45)	2.56 (2.55)	5.46 (5.46)	13.18 (13.82)	15
(II) C ₆ H ₅ BiBr ₂ ·Bipy	238–240	31.90 (31.92)	2.16 (2.18)	4.81 (4.65)	26.87 (26.54)	20
(III) C ₆ H ₅ BiI ₂ ·Bipy	212–213	27.46 (27.61)	2.00 (1.88)	3.88 (4.02)	36.12 (36.46)	^a
(IV) C ₆ H ₅ BiCl ₂ ·Phen	> 275	40.91 (40.24)	2.76 (2.44)	5.21 (5.21)	13.37 (13.20)	18
(V) C ₆ H ₅ BiBr ₂ ·Phen	> 275	34.44 (34.53)	2.10 (2.09)	4.48 (4.47)	25.10 (25.53)	18
(VI) C ₆ H ₅ BiI ₂ ·Phen	> 275	30.03 (30.02)	1.80 (1.82)	4.03 (3.89)	34.73 (35.25)	^a

^a Conductivity values varied with time.

The prepared compounds are listed in Table 1, along with analytical data. The compounds have various colours: (I) and (IV) are white; (II) and (V), pale yellow; (III) and (VI), orange-yellow. The chloride and bromide derivatives are slightly soluble in methylene chloride, acetonitrile, nitromethane, and insoluble in acetone and alcohols; (III) and (VI) are more soluble and can be recrystallized from acetone/pentane. All the compounds are insoluble in ether and hydrocarbons. All dissolve in pyridine, but this solvent clearly competes with Bipy and Phen in complexing with the phenylbismuthines.

Attempts to prepare the adducts of (C₆H₅)₂BiX (X = Cl, Br) with Bipy and Phen were unsuccessful. For example, the white solid, obtained by adding small quantities of pentane to an acetonitrile solution containing diphenylhalobismuthine and Bipy, (molar ratio 1/1), was identified as bipyridine (m.p. = 63–66°; melting point of the pure product 68–70°). The solvent was removed *in vacuo*; the solid residue was essentially the diphenylhalobismuthine.

Conductivity measurements were carried out in nitromethane and methylene chloride using an LKB Bridge. Data for nitromethane solutions are reported in Table 1. None of the compounds conduct in methylene chloride.

The UV-visible spectra of the bromo- and iodobismuthine complexes in methylene chloride, recorded with a Beckman DK-2A spectrophotometer, are shown in Figs. 1 and 2, along with the spectra of the related dihalobismuthines. The Figures

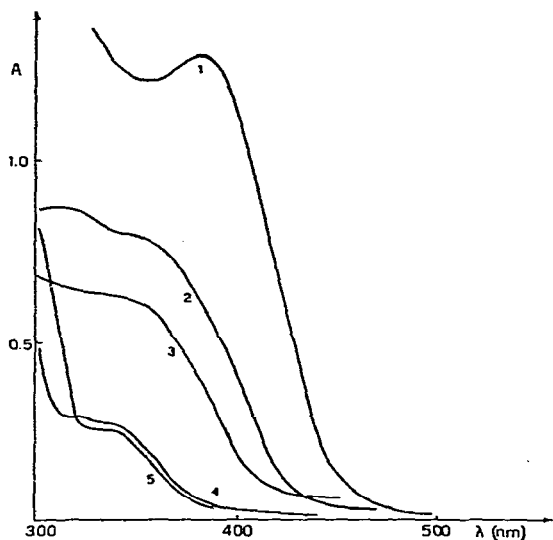


Fig. 1. Electronic spectra of $C_6H_5BiBr_2$ and the corresponding Phen and Bipy complexes: (1) $C_6H_5BiBr_2$, solid in Nujol; (2) $C_6H_5BiBr_2 \cdot Bipy$, solid in Nujol; (3) $C_6H_5BiBr_2 \cdot Phen$, solid in Nujol; (4) $C_6H_5BiBr_2 \cdot Phen$ in CH_2Cl_2 (conc. = $6.36 \times 10^{-5} M$); (5) $C_6H_5BiBr_2 \cdot Bipy$ in CH_2Cl_2 (conc. = $6.10 \times 10^{-5} M$).

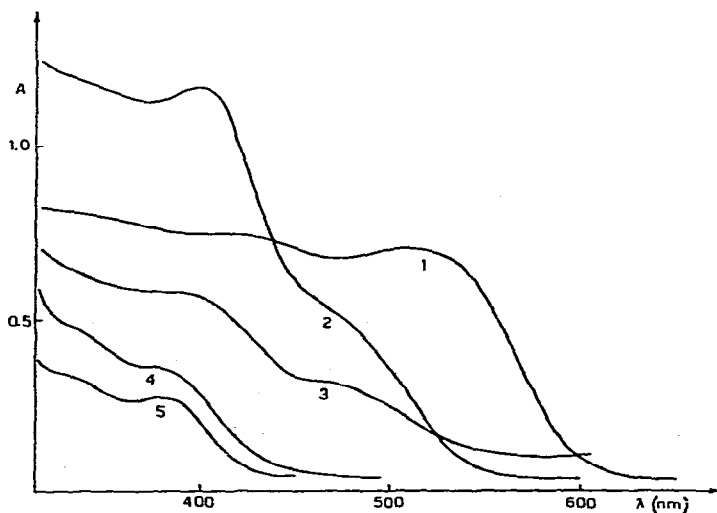


Fig. 2. Electronic spectra of $C_6H_5BiI_2$ and the corresponding Phen and Bipy complexes: (1) $C_6H_5BiI_2$, solid in Nujol; (2) $C_6H_5BiI_2 \cdot Phen$, solid in Nujol; (3) $C_6H_5BiI_2 \cdot Bipy$, solid in Nujol; (4) $C_6H_5BiI_2 \cdot Bipy$ in CH_2Cl_2 (conc. = $8.5 \times 10^{-5} M$); (5) $C_6H_5BiI_2 \cdot Phen$ in CH_2Cl_2 (conc. = $6.0 \times 10^{-5} M$).

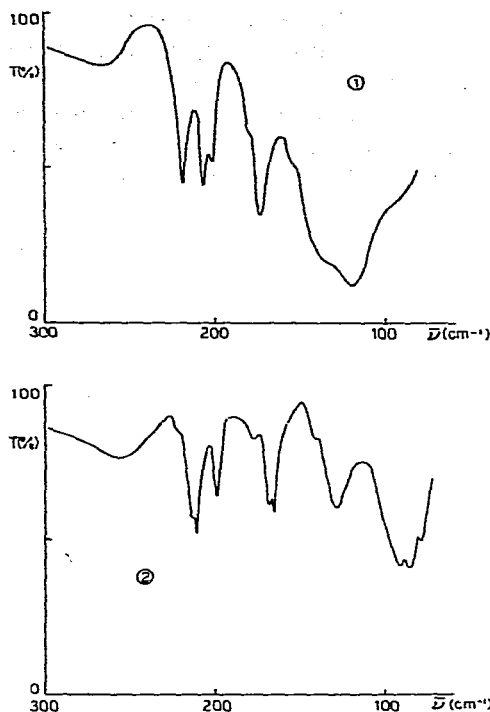


Fig. 3. Low energy infrared spectra of: 1) $C_6H_5BiBr_2$; 2) $C_6H_5BiI_2$, in Nujol mulls.

also show the spectra of the solid samples, finely ground in Nujol and spread on paper¹.

IR spectra, in Nujol and hexachlorobutadiene mulls, were measured on a Perkin-Elmer 621 Spectrophotometer ($4000-400\text{ cm}^{-1}$ CsI discs) and on a Beckman IR 11 Spectrophotometer ($400-80\text{ cm}^{-1}$ polyethylene discs). Low energy spectra are reported in Fig. 3-5.

Molecular weight measurements in CH_2Cl_2 were carried out with a Mechrolab Osmometer Model 302 (at 25°).

RESULTS AND DISCUSSION

The prepared compounds, listed in Table 1, are 1/1 adducts of $C_6H_5BiX_2$ ($X = Cl, Br, I$) with Bipy and Phen. They do not conduct in methylene chloride. The molecular weights in CH_2Cl_2 were measured for the phenyldiiodobismuthine adducts only: in fact the solubility of the chloro- and bromobismuthine adducts was too low for reliable data. The molecular weight values obtained for $C_6H_5BiI_2 \cdot Bipy$ [$C_{16}H_{13}N_2BiI_2$, found (calcd.), 678(696)] and $C_6H_5BiI_2 \cdot Phen$ [$C_{18}H_{13}N_2BiI_2$, found (calcd.), 698(720)] indicate that the complexes are monomeric in methylene chloride. The electronic spectrum of phenyldibromobismuthine in CH_2Cl_2 shows a maximum at 341 nm; the compound is monomeric in this solvent¹. In the solid state the maximum shifts to higher wavelengths (Fig. 1, number 1), probably because of the formation of Br bridges and thus weakening of the Bi-Br bond. The bands of the adducts in the solid state and in methylene chloride (Fig. 1) occur at frequencies higher than that found for phenyldibromobismuthine in the same conditions; the ligands do not

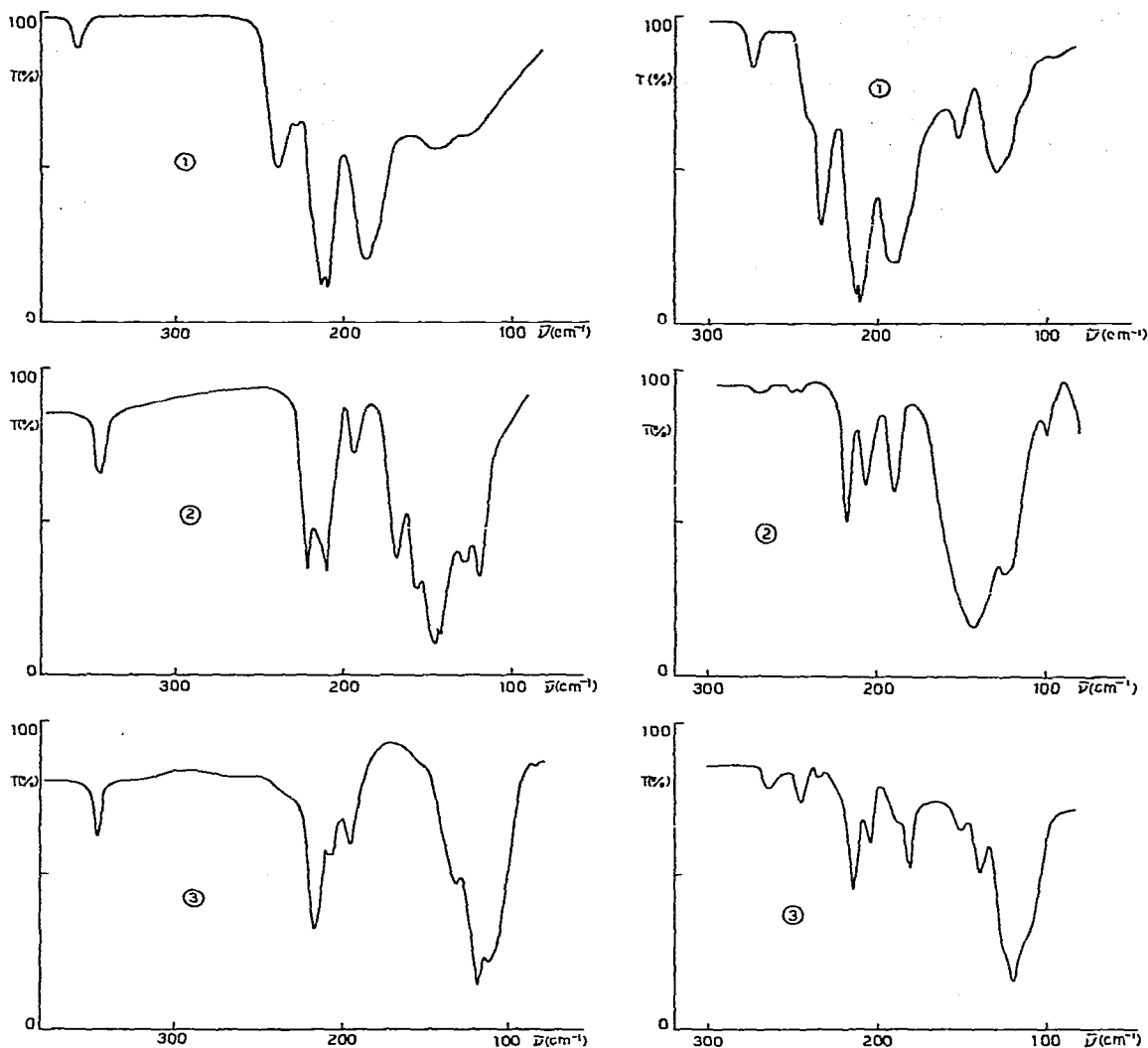


Fig. 4. Low energy infrared spectra of bipyridine adducts: 1) $C_6H_5BiCl_2 \cdot Bipy$; 2) $C_6H_5BiBr_2 \cdot Bipy$; 3) $C_6H_5BiI_2 \cdot Bipy$ in Nujol mulls.

Fig. 5. Low energy infrared spectra of phenanthroline adducts: 1) $C_6H_5BiCl_2 \cdot Phen$; 2) $C_6H_5BiBr_2 \cdot Phen$; 3) $C_6H_5BiI_2 \cdot Phen$, in Nujol mulls.

absorb at $\lambda > 330$ nm. The spectra confirm that in solution the bromobismuthine adducts do not decompose to the starting compounds; in the solid state complex formation leads to breaking of the Bi-Br bridges. The spectra of the iodobismuthine adducts (Fig. 2) show a similar behaviour; the spectra of the chlorobismuthine adducts are not reported because the charge-transfer band is covered by a band of the ligands having a high extinction coefficient (Bipy, $\epsilon(282 \text{ nm})$ 13,500; Phen, $\epsilon(265 \text{ nm})$ 25,000).

The complexes are slightly dissociated in nitromethane (Table 1). A weak dissociation was noticed for $C_6H_5BiBr_2 \cdot Bipy$ and $BiX_3 \cdot L$ ($L = Bipy, Phen$) in nitrobenzene³.

IR spectra of $C_6H_5BiX_2$ in the $4000-400\text{ cm}^{-1}$ region show the following peaks: $C_6H_5BiBr_2$: 3051 vw, 3031 w, 1568 vw, 1555 vw, 1465 m, 1425 m, 1320 vw, 1185 m, 1156 w, 1080 vw, 1047 m, 992 m, 711 s, 673 s, 432 m cm^{-1} . $C_6H_5BiI_2$: 3051 vw, 3031 vw, 1565 vw, 1557 vw, 1467 m, 1427 m, 1322 w, 1183 m, 1059 vw, 1046 vw, 992 m, 716 s, 681 s, 443 (sh), 438 m cm^{-1} . All the peaks can be assigned to vibrational modes of the phenyl group⁹. The low energy spectra of both the bismuthines are reported in Fig. 3. In this region triphenylbismuthine shows a large intense band with peaks at 216, 224, 236 cm^{-1} , assigned to phenyl-Bi vibrations⁹. In the halobismuthines the phenyl-Bi vibrations must contribute to the absorption around 200 cm^{-1} , while the Bi-halogen vibrational modes probably occur at about 120 cm^{-1} in $C_6H_5BiBr_2$ and about 90 cm^{-1} in $C_6H_5BiI_2$.

The low energy spectra of the Bipy and Phen complexes are shown in Figs. 4 and 5 respectively. In this region the free bipyridine absorbs at 256 vw, 166 s, 117 w, 94 s cm^{-1} , and the free phenanthroline at 258 w, 240 s, 150 m, 120 s cm^{-1} . The mono-phenylbismuthine adducts gives a number of bands not easily assignable, since the bands due to Bi-phenyl, Bi-nitrogen and Bi-halide vibrations should occur below 300 cm^{-1} . The Bi-Cl vibrations may contribute to the bands located at 233 cm^{-1} in $C_6H_5BiCl_2 \cdot Phen$ and at 239 cm^{-1} in $C_6H_5BiCl_2 \cdot Bipy$. The Bi-Br vibrations may contribute to the bands at about 140 cm^{-1} in both the adducts, and the Bi-I vibrations to the bands near 120 cm^{-1} .

The IR spectra of the adducts in the $1600-400\text{ cm}^{-1}$ region are consistent with coordinated Bipy and Phen¹⁰⁻¹³. The ring vibration bands, present in free Bipy at 1580 and 1558 cm^{-1} , move to higher frequencies in the adducts, and are independent of the halide (1597 w and 1591 m cm^{-1}). The strong band of free Bipy at 751 cm^{-1} , with a shoulder at 735 cm^{-1} , splits on coordination to 760 and 730 cm^{-1} ; the strong band at 402 cm^{-1} moves to 412 cm^{-1} in $C_6H_5BiCl_2 \cdot Bipy$, and to 410 cm^{-1} in $C_6H_5BiX_2 \cdot Bipy$ (X=Br, I). A weak band appears in the three complexes at 346-349 cm^{-1} . This band is not present in free Bipy, but has been found in the spectra of some complexes¹³.

The spectra of the phenanthroline adducts in the $1600-400\text{ cm}^{-1}$ region show slight variations from the spectrum of the ligand. The bands observed in free Phen at 1610, 1580 cm^{-1} move to higher frequencies in the three complexes (1620 m, 1590 m). The strong band at 848 cm^{-1} splits on coordination at $849 \pm 2, 861 \pm 2\text{ cm}^{-1}$; the bands at 622 and 408 cm^{-1} move to 642 and 418 cm^{-1} in $C_6H_5BiCl_2 \cdot Phen$, to 639 and 417 cm^{-1} in $C_6H_5BiBr_2 \cdot Phen$, and to 636 and 415 cm^{-1} in $C_6H_5BiI_2 \cdot Phen$. The first two compounds also show two weak bands at 498 and 472 cm^{-1} , and the last compound shows a weak band at 469 cm^{-1} ; these bands have been noticed in other complexes¹⁴. The bands due to the phenyl group occur in the adducts at about the same frequencies as in the free dihalobismuthines, and are easily identifiable.

The results enable us to conclude that in the adducts described Bipy and Phen act as bidentate ligands, and the bismuth atom has a coordination number of five. The diphenylhalobismuthines do not form adducts with the same ligands; this can be ascribed to the reduced ability of bismuth to act as an acceptor as the number of phenyl groups increases, and to steric interaction between the phenyl groups and the relatively large ligands.

The solid state structure of the phenyldihalobismuthines is not known. These compounds seem to be polymerized in the solid state, probably through halide bridges.

The far IR data show that the bands assigned to Bi-halide vibrations occur in the free phenyldihalobismuthines at frequencies lower than those of the corresponding adducts, whereas with an increase in the coordination number of the bismuth atom, and consequent increase in the ionic character of the Bi-halide bond, the Bi-halide vibrations would be expected to shift to lower frequencies in the adducts. Since different structures and different coordination numbers are probably involved in the solid state for the two sets of compounds, the vibrational frequencies cannot be correlated; even so, the results suggest that the phenyldihalobismuthines do not behave as discrete molecules in the solid state.

ACKNOWLEDGEMENTS

We are grateful to Mr. F. Madalosso and Mr. S. Sitran for technical assistance.

REFERENCES

- 1 G. Faraglia, *J. Organometal. Chem.*, 20 (1969) 99.
 - 2 R. Okawara, K. Yasuda and M. Inoue, *Bull. Chem. Soc. Jap.*, 39 (1966) 1823.
 - 3 W. R. Roper and C. T. Wilkins, *Inorg. Chem.*, 3 (1964) 500.
 - 4 F. I. Kupchik and G. T. Theisen, *J. Organometal. Chem.*, 11 (1968) 627.
 - 5 H. Gilman and H. L. Yablunsky, *J. Amer. Chem. Soc.*, 63 (1941) 207; H. Gilman and H. L. Yale, *Chem. Rev.*, 30 (1942) 281.
 - 6 J. F. Wilkinson and F. Challenger, *J. Chem. Soc.*, 125 (1924) 854.
 - 7 G. Peyronel, S. Buffagni and I. M. Vezzosi, *Gazz. Chim. Ital.*, 98 (1968) 147, 156.
 - 8 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford (1966).
 - 9 K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, 17 (1963) 1875.
 - 10 A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, 9 (1959) 211.
 - 11 S. P. Sinha, *Spectrochim. Acta*, 20 (1964) 879.
 - 12 J. R. Ferraro, L. J. Basile and D. L. Kovacic, *Inorg. Chem.*, 5 (1966) 391.
 - 13 R. J. Clark and C. S. Williams, *Spectrochim. Acta*, 21 (1965) 1861.
 - 14 S. J. Jain and R. Rivest, *Inorg. Chim. Acta*, 2 (1970) 291.
- J. Organometal. Chem.*, 44 (1972)