splitting of the band as a result of distortion. The values of this parameter have been reported by Nadezhina and Kovalenko, the position of lowest transition, $E_g \rightarrow T_{1g}$, being in the region 317-550 cm$^{-1}$. The value of Racah's parameter $B$ calculated following strong-field coupling (in the range 1-918-2,186) indicates an increase in covalency. The values of $9Dq$ (difference of $v_3$ and $v_1$ transition in strong field) for these mixed ligand complexes are in the range 1.9184-2.1868. Electronic spectral data and calculated values for parameter $B$ and $9Dq$ in cm$^{-1}$ for cobalt(II) complexes are presented. The magnetic moment of metal through sulphur atom of thiourea ligand, $\mu$ ($\mu g$), in the range 9.10-10.650 is normally low indicating increase in covalency. The values of $v_3$ and $v_1$ (transition, $\mu$) are in the range 317-550 cm$^{-1}$ for cobalt(II) complexes. Naturally its contribution towards nephelauxetic ratio, $g$ (0.35 to 0.56) is low indicating increase in covalency. The values of $\beta$ (C-N) and $v_3$ (transition in strong field) for these mixed ligand complexes are in the range 9770 to 11928 cm$^{-1}$ and that of $v_3/v_1$ ratio in the range 1.9184-2.1868. Electronic spectral data and calculated values for parameter $B$ and $9Dq$ (in cm$^{-1}$) and $v_3/v_1$ ratio are given in Table 2.

The value of magnetic moment ($\mu_{eq}$) of the complexes are in the range 1.74 to 1.95 B.M., suggesting the presence of one unpaired electron and hence complexes are spin paired complexes. However, the diphenylthiourea derivative has been found to be diamagnetic. The diamagnetic nature of this complex may be due to metal-metal bond.

Infrared spectrum of diaquo-bis-dimethylglyoximato-cobalt(II) exhibits coordinated water molecules at 3440 cm$^{-1}$. This band is absent in the presently prepared complexes, indicating these to be anhydrous. The changes in $v$ (M-N) occur around 510 cm$^{-1}$, while absorption due to $v$ (C-N) ($\approx$1070 cm$^{-1}$) and $v$ (N-O) (1540-1580 cm$^{-1}$) undergo slight shift from similar absorption in parent complex. The bands of dimethylglyoxime and thioureas are modified, indicating that both the ligands are bonded to metal. According to Bailey and Pearson, large increase in $v$ (C-N) and amide-II vibrations and small shift in $\delta$ (NH$_2$) vibration indicate S-bonding to metal ion. In the present complexes the shift in $v$ (N-H) by 10-60 cm$^{-1}$, in amide-II vibrations by 15 cm$^{-1}$ and in $\delta$ (NH$_2$) vibration by 3-5 cm$^{-1}$ support the coordination of metal through sulphur atom of thiourea ligand.

The authors thanks Prof. R. C. Kapoor for facilities and the UGC, New Delhi, for the award of a fellowship (to D.S.S.).

References

**Synthesis & Characterization of Some Dibutylnmetal(III) Pseudohalides**

T. N. SRIVASTAVA & KIRAN KAPOOR

Chemistry Department, Lucknow University

Lucknow 226007

Received 12 October 1978; accepted 3 November 1978

Some hitherto unknown pseudohalides of the formula Bu$_n$MX (M= Ga, In or TI; X=N$_3$, NCO or NCS) have been synthesized in quantitative yield through metathetical reaction between Bu$_2$MCl and the corresponding alkali metal salts. The compounds have been characterized by their elemental analyses and IR data. The azides are thermally stable and do not explode at their melting points. Infrared data are presented in support of their structures.

As compared to extensively studied pseudohalides of non-transition metals of Group IV$^+3$ (R$_2$MX, R = an organic group; X = N$_3$, NCO or NCS, M = Ge or Sn), similar compounds of Group III metals (R$_2$MX, M = Ga, In or TI) have received little attention. Mueller et al. reported the preparation of some dialkyl azides of aluminium, gallium, indium and thallium by the interaction of chlorine azide with corresponding metal trialkyls. Srivastava and coworkers reported the preparation and characterization of some diaryl thallium cyanides, azides and selenocyanates. Infrared studies of R$_2$TINCS (R = Me, Et or Ph) and PhTl (N$_3$)$_2$ have also been reported. We now report the synthesis and characterization of some dibutylnmetal(III) pseudohalides, Bu$_2$MX (M = Ga, In or TI; X = N$_3$, NCO, NCS, NCS).

Dibutylgallium, indium and thallium chlorides were prepared by the interaction of metal(III) chlorides and dibutyltin dichloride.

In a typical experiment, to a boiling solution containing a mixture of dibutyltin dichloride (1 mmol) and tetrahydrated metal(III) chloride in 40 ml methanol/ethanol, was added aqueous sodium hydroxide (30 ml, 20%) and the mixture refluxed. The resulting mixture was cooled and hydrochloric acid (60 ml, 15%) added with constant stirring. The solid product was filtered, washed with ethanol and finally with diethyl ether and dried at 90°. The product was recrystallized from the same solvent.

Dibutylnmetal(III) pseudohalides were obtained by stirring dibutylnmetal chloride with the corresponding alkali metal salt, at room temperature, in pyridine-water (1:1) mixture for 1 to 3 hr. The solid was filtered, washed with ethanol-water and dried in vacuo.

All the pseudohalides have been prepared through metathetical reaction Bu$_2$MCl$+M'X \rightarrow$Bu$_2$MX$+$...
M'Cl (M = Ga, In or Tl; X = N₃, NCS, NCO, or NCSe; M' = Na, K or NH₄).

All the compounds listed in Table 1 are white crystalline solids, stable at room temperature, except the cyanates and dibutylthallium selenocyanate which slowly decompose on standing. They are insoluble in common organic solvents.

The azides are thermally stable and do not explode at their melting points. The chalcogenates NCX (X = O, S or Se) are capable of bonding to metal atom either through N or X. They give rise to three fundamental vibrations of the presently studied pseudohalides are listed in Table 1 indicate their iso-structure with a deformation mode of NCX. These peak positions of the presently studied pseudohalides are listed in Table 1 indicate their iso-structure with M-N bonding similar to corresponding organotin derivatives.

Dibutylmetal(III) azides show a sharp and strong band at 2040 ± 10 cm⁻¹ which is close to the absorption occurring in similar compounds, such as those of ammonium and potassium at 2050 and 2040 cm⁻¹ respectively. A second band of weak intensity located a 1325 ± 5 cm⁻¹ is assigned to N=NC=N symmetric mode of vibration. The banding mode of vibration has been identified at 655 ± 5 cm⁻¹. The spectral data therefore suggest an ionic character of the dibutylmetal(III) azides in contrast to the heavy metal ionic azides. The abnormally high stability of dibutylmetal(III) azides may be attributed to dative π-bonding from nitrogen to metal atom as shown below.

Bu₄M-N=N=NC≡N = Bu₄M-N=N=NC≡N

The absorptions of strong intensities at 600, 585 and 570 cm⁻¹ are assigned to Ga-C, In-C and Tl-C stretching modes respectively. The absorption bands of medium to weak intensities at 370 and 350 cm⁻¹ may be assigned to Ga-N, In-N and Tl-N stretching respectively.

The authors thank the State Council of Science and Technology, UP, for financial assistance to one of them (K.K.).

References