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Cobalt(II) Complexes with 1,8-Naphthalenebis(dimethylarsine)

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The ligand 1,8-naphthalenebis(dimethylarsine), symbolized as Nas, reacts with Ni(II), Pd(II) and Pt(II) (M) giving compounds of different stoichiometries depending on the anion and the reaction conditions. Five-coordinated complexes of general formula $M(Nas)_2X_2$, where X = Cl, Br. I, SCN, have been isolated, and five- and/or four-coordinated when X = ClO_4, NO_3. Further adducts of formula $MNasX_2$, where X = Cl, Br, I, SCN have been also obtained [1–4]. With $TiCl_4$ and $NbCl_4$, Nas has been reported to form eight-coordinated complexes of the type $Ti(Nas)_2Cl_4$ and $Nb(Nas)_2Cl_4$ [5]. The ligating behaviour of Nas towards the above metals is similar to that of *o*-phenylenebis(dimethylarsine), Das, [6], although Nas forms six-membered instead of five-membered chelated rings. In the Nas complexes a lowered symmetry produces in the d–d region different electronic spectra which could be rationalized in terms of As–As distances (2.49 Å for Nas, 3.21 Å for Das) and bond angles.

Much experimental evidence is available concerning the synthesis and characterization of the complexes of bi- and ter-valent cobalt with Das [7–13], whereas no complexes with Nas have been so far described. It therefore seemed of interest to prepare the complexes of this ligand for comparison purposes.

This communication reports preliminary data on some cobalt(II) complexes.

Experimental

The ligand Nas was prepared from 1,8-dichloronaphthalene and sodiumdimethylarsine in tetrahydrofuran, as previously described [14].

Preparation of the Complexes

$[Co(Nas)_3][CoX_4]$ (X = Cl, Br)

An ethanol solution of $CoX_2 \cdot 6H_2O$ (3 mmol) and the ligand (5 mmol) was refluxed for 1 hour. Upon cooling the solution deposited green crystals of the complex which were filtered, washed with ethanol and ethyl ether and dried *in vacuo* over P_2O_5.

$[Co(Nas)_3](ClO_4)_2$

An ethanol solution of $Co(ClO_4)_2 \cdot 6H_2O$ and the ligand in stoichiometric amounts was refluxed for 0.5 hours giving a yellow precipitate, which was filtered, washed with ethanol and ethyl ether and dried *in vacuo* over P_2O_5. The crude product was recrystallized from methanol.

$[Co(Nas)_2I]I$

To an ethanol solution of the ligand (6 mmol), $CoI_2 \cdot 6H_2O$ (3 mmol) was added under stirring at room temperature. Green crystals of the complex precipitated and were filtered, washed with ethanol and ethyl ether and dried *in vacuo* over P_2O_5.

$[Co(Nas)_2I]ClO_4$

To a suspension of LiI in acetone, $[Co(Nas)_3](ClO_4)_2$ in boiling ethanol was added. By refluxing for 0.5 hours the solution deposited a green compound which was filtered, washed with ethanol and dried *in vacuo* over P_2O_5.

All the preparations were carried out under a nitrogen atmosphere.

The measurements of the magnetic susceptibilities of the complexes were obtained at room temperature with the Gouy method. The conductivities of 10^{-3} *M* nitromethane solutions of the complexes were measured at 25 °C by an LKB Conductivity Bridge Mod. 3216 B. The electronic spectra in the 360–700 nm region were taken at 25 °C by a Beckman DK2A Spectrophotometer. The infrared spectra in the 4000–400 cm^{-1} region were recorded on a Perkin-Elmer Mod. 621 Infrared Spectrophotometer using Nujol mulls betweeen KBr windows, and in the 500–150 cm^{-1} region on a Beckman IR 11 Spectrophotometer using Nujol mulls between polythene windows.

Results and Discussion

The ligand Nas with $CoX_2 \cdot 6H_2O$ (X = Cl, Br) gives green complexes for which, on the evidence of the electronic spectra (Table I), the structural formula $[Co(Nas)_3][CoX_4]$ would be assigned in the solid state. Accordingly, the far IR spectra exhibit

TABLE I. Analytical Data[a], Effective Magnetic Moments and Electronic Spectra[b] of the Complexes.

Compounds	M.p. (°C)	C%	H%	Hal%	As%[c]	Co%	μ_{eff} (B.M.)	Electronic Spectra	
								MeNO$_2$	Solid
[Co(Nas)$_3$][CoCl$_4$]	218–20	39.3	4.3	11.2	35.6	9.6	3.56[d]	6.4 (70)	
		(39.8)	(4.3)	(11.2)	(35.5)	(9.3)		14.9 (770)	14.6
								15.4sh (730)	15.0
								16.9 (510)	16.9
[Co(Nas)$_3$][CoBr$_4$]	245	34.4	3.7	22.4	31.1	8.7	3.50[d]	6.2 (65)	
		(34.9)	(3.7)	(22.1)	(31.1)	(8.1)		14.5 (830)	14.4
								14.9 (840)	15.0
								16.1sh (600)	15.7
[Co(Nas)$_3$](ClO$_4$)$_2$	205–7	40.0	4.2	5.9	35.5	4.5	diamagnetic	25.5 (3000)	25.5
		(39.8)	(4.3)	(5.6)	(35.5)	(4.7)			
[Co(Nas)$_2$I]I	229	34.1	3.8	25.7	30.3	6.0	2.06		12.5
		(34.1)	(3.7)	(25.8)	(30.4)	(6.0)		15.7 (670)	15.6
								22.8 (2100)	23.2
[Co(Nas)$_2$I]ClO$_4$	244–6	35.3	3.8	3.3[e]; 13.2[f]	31.5	5.8	1.97	15.7 (670)	15.6
		(35.1)	(3.8)	(3.7); (13.3)	(31.3)	(6.1)		22.8 (2100)	23.0

[a] The calculated values are in parentheses. [b] $\bar{\nu}_{max} \times 10^{-3}$ cm^{-1} (ϵ_{mol}). [c] Arsenic was determined as described [15]. [d] μ_{eff} per cobalt atom is given. [e] Cl%. [f] I%.

the ν(Co–X) band at 290 cm^{-1} for the chloro- and 230 cm^{-1} for the bromo-derivative, typical of the [CoX$_4$]$^{2-}$ species [16]. Both the complexes are paramagnetic ($\mu_{eff} \cong 3.5$ B.M. for Co atom, Table I): since the value for the tetrahedral cobaltate ion is in the range of 4.7 B.M. [17], the moment of [Co(Nas)$_3$]$^{2+}$ ion would be around 2 B.M., as expected for a d^7 low-spin configuration. The complexes dissolve in ethanol or nitromethane to eventually form brown solutions, from which unstable compounds separate. The analytical data suggest empirical formulae identical to those of the green derivatives, but the IR and visible spectra do not give any evidence of the tetrahedral anion [CoX$_4$]$^{2-}$. The low stability of the compounds in the solid state and in solution did not allow us to obtain further information.

By reacting Nas and CoI$_2$·6H$_2$O the complex [Co(Nas)$_2$I]I was prepared. The compound behaves as an uni-univalent electrolyte and shows spectral and magnetic analogues with other low-spin five-coordinated complexes of cobalt(II) [18]. For this reason we propose a structure with one iodine atom bonded to the metal, the second being external to the complex.

The complex [Co(Nas)$_3$](ClO$_4$)$_2$ exhibits in the Cl–O stretching region one band at 1080 cm^{-1}, indicative of the presence of free perchlorate ion [19]. The compound is a bi-univalent electrolyte in nitromethane solution; by reaction with sodium tetraphenylborate in absolute ethanol the analogous [Co(Nas)$_3$][B(C$_6$H$_5$)$_4$]$_2$ was obtained. Surprisingly, both the complexes are diamagnetic. Explanations for this magnetic behaviour are difficult: some Co(II)–Co(II) bond interaction *via* coupling of the unpaired electrons should be possible, as already suggested for the diamagnetic [Co(Das)$_2$(H$_2$O)]$_2$(ClO$_4$)$_4$ [13], so that not all the ligand molecules would act as bidentate. It is noteworthy that [Co(Nas)$_3$](ClO$_4$)$_2$ reacts in ethanol or acetone with LiI to give the five-coordinated complex [Co(Nas)$_2$I]ClO$_4$, similar to [Co(Nas)$_2$I]I on the basis of spectral, conductivity and magnetic evidence (Table I).

In conclusion it appears that the ligand Nas would have in respect to Das a more pronounced tendency to form five-coordinated cobalt(II) complexes and in particular to stabilize the metal in its lower oxidation state.

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