Transition-metal Complexes Containing an As-donor Positively-charged Ligand

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Summary A novel series of cobalt(II) and nickel(II) complexes containing the monoquaternized ditertiary arsine, $Ph_2AsCH_2CH_2As^+Ph_2(CH_2Ph)$ have been prepared.

COMPLEXES of positively-charged amines with Co^{II} and Ni^{II} have been extensively investigated,[1–5] and some similar complexes of positively-charged tertiary phosphines are also known.[6,7] An investigation of the donor properties of positively-charged tertiary arsines appeared to be particularly interesting in view of the extreme versatility of As-donor ligands with nontransition as well as with transition elements in a variety of oxidation states and stereochemistries. The ligand $Ph_2AsCH_2CH_2As^+Ph_2$-(CH_2Ph) (abbreviated as L^+) was first chosen for this

TABLE. *Colours and* d-d *electronic spectra of* Co^{II} *and* Ni^{II} *complexes containing a positively-charged arsine ligand*

Complex[a] and colour	*d-d* Electronic absorptions[b] Midpoint of band ($\text{cm.}^{-1} \times 10^{-3}$)[c]	Assignment[d]	
$[CoBr_3(L^+)]$	4·4	$^4A_2(F) \rightarrow$	$^4A_1(T_1, F)$
blue	7·2		$^4E(T_1, F)$
	14·5(13·8, 15·9)[e]		$^4A_2, {}^4E(T_1, P)$
$[CoI_3(L^+)]$	4·1	$^4A_2(\mathrm{F}) \rightarrow$	$^4A_1(T_1, F)$
greenish-tan	7·0		$^4E(T_1, F)$
	13·5(12·8, 13·5, 14·6)[f]		$^4A_2, {}^4E(T_1, P)$
$[NiCl_3(L^+)]$	4·9	$^3E(\mathrm{T}_1, F) \rightarrow$	$^3E(T_2, F)$
blue	5·9[g]		$^3A_1(T_2, F)$
	8·7		$^3A_2(F)$
	15·6(14·8, 16·4)		$^3E, {}^3A_2(T_1, P)$
$[NiBr_3(L^+)]$	4·8	$^3E(T_1, F) \rightarrow$	$^3E(T_2, F)$
turquoise	5·8		$^3A_1(T_2, F)$
	8·4[h]		$^3A_2(F)$
	15·0(13·9, 15·7)		$^3E, {}^3A_2(T_1, P)$
$[NiI_3(L^+)]$	4·8	$^3E(T_1, F) \rightarrow$	$^3E(T_2, F)$
brown	5·6		$^3A_1(T_2, F)$
	8·2(8·5, 7·3)		$^3A_2(F)$
	13·2		$^3E, {}^3A_2(T_1, P)$

[a] $L^+ = Ph_2AsCH_2CH_2As^+Ph_2(CH_2Ph)$. [b] From diffuse reflectance spectra. [c] Values in parentheses indicate partly resolved maxima. [d] According to energy level diagram of ref. 8, for pseudo-tetrahedral d^7 and d^8 systems in fields of C_{3v} symmetry. [e] Also shoulders at 17·2, 19·0. [f] Also shoulders at 15·6, 17·2. [g] With shoulder at 10·2. [h] With shoulder at 9·5.

investigation because parallel work on positively-charged N-donor ligands had shown that when a chain of two CH_2 groups is interposed between the donor atom and the positively-charged site, the positive charge begins to affect appreciably the donor properties of the ligand.[1] The metal ions Co^{II} and Ni^{II} appeared to be particularly suitable since their relatively low tendency to π-back-donation should allow a direct comparison of the properties of positively-charged As-donor and N-donor ligands.

Our results show that the cation $Ph_2AsCH_2CH_2As^+Ph_2$-(CH_2Ph) co-ordinates to Co^{II} and Ni^{II} halides to form complexes of the general formula $MX_2,(L^+)X$. On the basis of their magnetic properties, and electronic and vibrational spectra these complexes can be formulated as the species $[MX_3(L^+)]$, in which the central metal ion has a high-spin electron configuration and a pseudo-tetrahedral stereochemistry with C_{3v} symmetry. Some representative complexes† of this type are listed in the Table, together with their characteristic colours and electronic *d-d* absorptions. It is interesting to observe that the electronic spectra of these complexes, while indicative of an approximately tetrahedral ligand environment, can be assigned satisfactorily only on the basis of a crystal-field model of C_{3v} symmetry.[8] The splitting of the $^4T_1$ term observed for the Co^{II} complexes is of the magnitude expected on the basis of the relative positions of the arsenic and halogeno-ligands in the spectrochemical and nephelauxetic series, and is comparable to that observed for the $[MX_3(L^+)]$ complexes of N-donor[4] and P-donor[6,7] ligands. The $[MX_3(L^+)]$ complexes with $(L^+) = Ph_2AsCH_2CH_2As^+Ph_2(CH_2Ph)$ are markedly stable in the crystalline state, decomposing only above 200°, and appear to be fairly stable in solutions of non-co-ordinating solvents. We are unaware of examples of similar high-spin Co^{II} and Ni^{II} complexes containing uncharged monodentate tertiary arsines, and in fact only very few complexes of this type have been reported even with uncharged tertiary amine and phosphine ligands. Thus it appears that the presence of the positive charge on the arsine ligand $(L^+) = Ph_2AsCH_2CH_2As^+Ph_2(CH_2Ph)$ plays an important role in the stabilization of the novel class of complexes of formula $[MX_3(L^+)]$.

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† Correct analyses were obtained for all compounds.

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