Transition-metal Complexes of a Mixed Selenium–Sulphur Ligand

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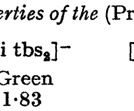
THE bis-1,2-dithiolene complexes have been much studied[1–4] because of the apparent stabilization of the square-planar geometry for a variety of transition-metal ions and because of the relatively easy and reversible oxidation and reduction reactions which these complexes undergo. These unusual properties have been shown to indicate extensive delocalization of the π-systems in these chelates and it has been suggested that some positive inter-donor-atom bonding interactions also help in the stabilization of both the bis- and tris-1,2-dithiolene complexes.[5] In order to examine these factors more closely and study the co-ordinating properties of selenium-donor chelating agents, we have synthesized and characterized a new series of square-planar bis-complexes containing the novel mixed selenium–sulphur ligand system (I) (tbs), in which inter-donor-atom interactions should be enhanced. The tbs ligand is the first example of a mixed selenium–sulphur chelating agent in which extensive π-delocalization is possible.[6]

The disodium salt of tbs (I) was prepared by the Na–liquid NH_3 reduction of *o*-methylthioselenoanisole (II) which was identified by its two methyl proton singlets, the first at τ7·6 for the *S*-CH_3 protons and the second at τ7·8 for the *Se*-CH_3 protons. The corresponding *o*-mercaptoselenophenol (III) was then generated by dissolving Na_2 tbs in an aqueous solution and acidifying to a pH of ~3. An n.m.r. spectrum of (III) in $CDCl_3$ showed a broad resonance at τ7·2 which split into two sharp resonances of approximately equal intensity at τ6·2 and 8·2 upon the introduction of HCl vapour into the sample. The resonance at τ8·2 is assigned as the selenol hydrogen resonance while that at τ6·2 is assigned to the thiol hydrogen. The series of monoanionic complexes $[\mathrm{M\ tbs_2}]^-$ for M = Ni, Cu, and Co, was prepared by the reaction of the potassium salt of (I) with the corresponding bivalent transition-metal halide in ethanol solution. In all cases, the initial formation of the bis-dianionic complex was followed rapidly by aerial oxidation to the monoanionic species. The complexes were isolated as their $\mathrm{Pr^n{}_4N^+}$ salts and were recrystallized from dichloromethane. The magnetic susceptibility data (Table) indicate that in the solid, the Cu complex has a spin singlet ground state, the

(I)



(tbs^{2-})

Physical properties of the $(\mathrm{Pr^n{}_4N})[\mathrm{M\ tbs_2}]$ *complexes*

	$[\mathrm{Ni\ tbs_2}]^-$	$[\mathrm{Co\ tbs_2}]^-$	$[\mathrm{Cu\ tbs_2}]^-$
Colour	Green	Blue	Green
μ_{eff} (B.M.)[a] ..	1·83	3·26	diamag.
$E_{\frac{1}{2}}$ (v)[b] for $\mathrm{ML_2{}^{2-} \rightleftharpoons ML_2{}^- + e^-}$	−0·53	−0·90	−0·70

[a] Solid-state magnetic susceptibilities determined by the Gouy method using $\mathrm{Hg[Co(SCN)_4]}$ as calibrant.

[b] Measured in dimethylformamide solution relative to a saturated calomel electrode.

Ni complex a spin doublet ground state, and the Co complex a spin triplet ($S = 1$) ground state. These results are in close agreement with those found for the analogous benzenedithiolate and methyl-substituted benzenedithiolate complexes.[2] The spin triplet [Co tbs$_2$]$^-$ complex is another unusual example of a stable high-spin square-planar complex.

The polarographic half-wave potentials for the reduction $ML_2^- + e^- \rightleftharpoons ML_2^{2-}$ (Table) are in good agreement with the analogous half-wave potentials of −0·55, −0·88, and −0·64 v for the Ni, Co, and Cu complexes, respectively, of the closely related ligand system benzene-1,2-dithiolate.[2] The monoanions [Ni tbs$_2$]$^-$ and [Cu tbs$_2$]$^-$ were reduced chemically to the dianions by hydrazine in de-gassed ethanol solutions under a nitrogen atmosphere. No analytically pure samples of the dianions have yet been isolated. The Co, Ni, and Cu monoanions exhibit rich and complex electronic spectra which agree reasonably well with those of the corresponding bisdithiolato-complexes.[2–4,7] Although it is clear that the [M tbs$_2$]$^-$ systems possess planar molecular geometries and electronic structures analogous to those of the bis-1,2-dithiolene complexes, the [M tbs$_2$]$^-$ complexes may exist as either *cis*- or *trans*-isomers and structural studies have been commenced to determine if one geometrical isomer is preferred.

The e.s.r. spectrum of the [Ni tbs$_2$]$^-$ complex was recorded at room temperature and at 100°K in dimethylformamide–CHCl$_3$ glass. The glass-medium spectrum shows three well separated principal g-values with significantly greater anisotropy in the g-tensor than is observed for the [Ni tdt$_2$]$^-$ complex.[7] For [Ni tbs$_2$]$^-$: $g_{zz} = 2{\cdot}034$, $g_{yy} = 2{\cdot}086$, $g_{xx} = 2{\cdot}228$, and $<g> = 2{\cdot}116$;[8] for [Ni tdt$_2$]$^-$:[7] $g_{zz} = 2{\cdot}016$, $g_{yy} = 2{\cdot}048$, $g_{xx} = 2{\cdot}183$, and $<g> = 2{\cdot}082$.[8] These results are similar to those observed by Davison and Shawl for the Ni[Se$_2$C$_2$(CF$_3$)$_2$]$_2^-$ complex.[6a] The increase in g-tensor anisotropy for the selenium systems apparently results from the greater spin–orbit coupling of the heavier donor atoms.[9] Hyperfine splitting due to natural abundance ^{77}Se (7·5%, $I = 1/2$) is observed on the high-field resonance with a hyperfine coupling constant A_{zz} of 61 ± 2 gauss. The low-field resonance indicates the possible presence of unresolved ^{77}Se hyperfine structure. However, since this hyperfine splitting was apparently not observed in the Ni[Se$_2$C$_2$(CF$_3$)$_2$]$_2^-$ spectrum, it is possible that both *cis*- and *trans*-isomers of [Ni tbs$_2$]$^-$ exist in the glass with only g_{xx} differing very significantly between the two isomers.

We thank the National Science Foundation for support of this research, and Drs. P. Rieger, A. Davison, and E. Stiefel for helpful comments regarding the e.s.r. data.

(*Received, January 24th,* 1969; *Com.* 105.)

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