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Synthesis and Structural Characterization of a New Series of Binuclear Cobalt(III) Complexes with Cyanides

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Babaeva and Baranovskii[1] reported the synthesis of $[Co(CN)_2(NH_3)_2(OH_2)_2]Cl$. However, we had a suspicion about the structural formula of this compound because of the very low solubility of the chloride in water and of the lack of absorption spectrum. Hence, we re-examined the route to this compound below and found that this is not monomeric, but dimeric in its configuration, *i.e., cis*(C)-*cis*(N)*trans*(O)-$[\{Co(CN)_2(NH_3)_2(OH_2)\}_2OH]Cl\cdot 4H_2O$ on the basis of the spectral and elemental analyses (henceforth, this compound is abbreviated as the complex (I)):

$$\mathit{cis}(S)\text{-}NH_4[Co(NH_3)_4(SO_3)_2]\cdot 3H_2O\,[2] \xrightarrow{NaCN} \mathit{cis}(C)\mathit{cis}(S)\mathit{trans}(N)\text{-}Na_3[Co(CN_2)(NH_3)_2(SO_3)_2]\cdot 4H_2O \xrightarrow{HCl} [\{Co(CN)_2(NH_3)_2(OH_2)\}_2OH]Cl\cdot 4H_2O.$$

The evidence from which we drew this conclusion is provided with the fact that the molar ratio of cobalt to chloride is invariably 2:1; the calculated chloride content (14.08%) for the monomeric formula is almost double that (7.87%) for the dimeric one. In agreement with that for the latter, the observed value was 7.66%.

Figure 1 shows the absorption spectra of the complex (I) and its derivatives in DMSO (dimethyl sulfoxide). The second band for the complex (I) exhibits a large intensity ($\log \epsilon = 3.84$) and a broad feature in width, both characteristic of usual binuclear cobalt(III) complexes rather than of the mononuclear ones of the $[CoC_2N_2O_2]$ type, suggesting it to be dimeric in its configuration, even if we take account of the possibility that the coordinated water might be replaced with DMSO molecules in DMSO.

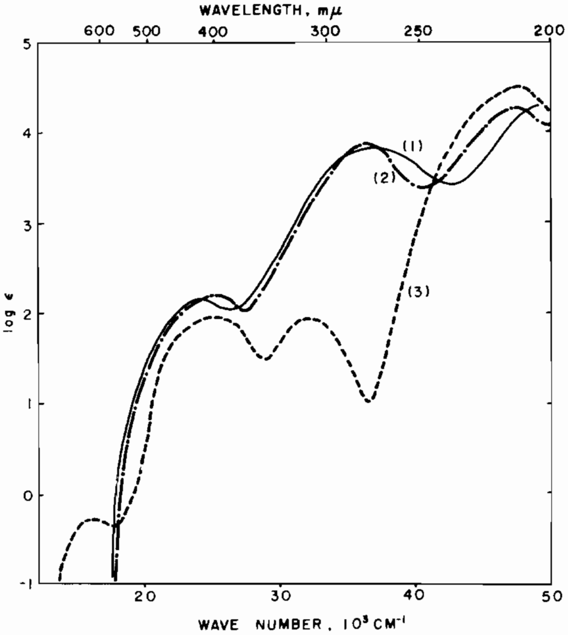

Fig. 1. Absorption spectra of binuclear and mononuclear cobalt(III) complexes: (1) ——— $[\{Co(CN)_2(NH_3)_2(OH_2)\}_2OH]Cl\cdot 4H_2O$ in DMSO; (2) – · – · – $[\{Co(CN)_2en(OH_2)\}_2OH]ClO_4\cdot 2H_2O$ in DMSO; (3) ‐ ‐ ‐ ‐ *cis*-$[Co(CN)_2en_2]Cl$ in H_2O.

This assignment is reinforced by the preparation and characterization of several novel binuclear complexes of similar type as follows: $[\{Co(CN)_2(NH_3)_3\}_2OH]ClO_4\cdot 3H_2O$, $[\{Co(CN)_2dien\}_2OH]ClO_4\cdot 3H_2O$, $[\{Co(CN)_2en(OH_2)\}_2OH]ClO_4\cdot 2H_2O$, $[\{Co(CN)_2tn(OH_2)\}_2OH]OH\cdot 4H_2O$. These complexes were prepared from the complex (I) by substitution reactions with basic ligands at 0 °C except for the reaction with ammonia.

The low temperature reaction with basic ligands (en or tn) makes it possible to substitute preferentially and selectively the two counter ammonia ligands with regard to two cyanides (*cis*) around the cobalt within the complex (I). This can be explained fully in terms of the "*trans* influence",[3] *i.e.,* the counter bond weakening effect of the cobalt–cyanide linkage.[4] The first ethylenediamine can readily enter the coordination sphere still at 0 °C, but the second one cannot, even if an excess of ethylenediamine was used, suggesting that the remaining oxygen donors are situated at *trans* sites each other.

On the other hand, the high temperature reaction (40 - 90 °C) of the complex (I) with basic ligands yielded the mononuclear complexes of the type *cis*-$[Co(CN)_2N_4]$ (N_4 = en_2, pn_2, tn_2, or trien).*

The complex (I) reacted with ammonia (38%) at 40 - 50 °C for 2 hr to give rise to $[\{Co(CN)_2(NH_3)_3\}_2OH]Cl\cdot 3H_2O$.

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*pn = propylenediamine; tn = trimethylenediamine; trien = triethylenetetramine; dien = diethylenetriamine.

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