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WATER SOLUBLE ALKYL-COBALT CHELATES AS ORGANOMETALLIC COMPLEX CATIONS

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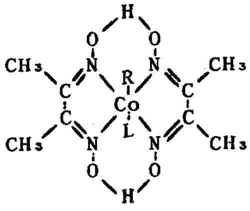
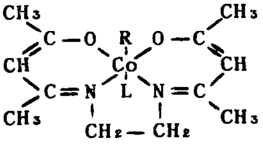
Dimethylglyoxime[1] (A) and, more recently, bis(acetylacetone)ethylendiimine[2] (B) and bis(salicylaldehyde)ethylendiimine[3] (C) were used to obtain cobalt(III) chelates which can give stable organo-cobalt derivatives.



A



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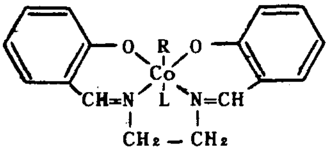
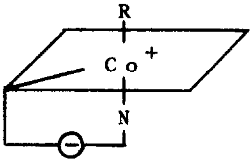


C

From known structures of nickel, copper, cobalt, platinum dimethylglyoxime[4] and the Co bis(salicylaldehyde)ethylendiimine[5] the arrangement of chelate rings in the above complexes is assumed to be approximately in the equatorial plane of an octahedral structure, the axial ligands being the organic group R and a Lewis base L.

The unusual stability of the metallorganic derivatives can be attributed to the proper adjustment of the charge on the cobalt atom, due to the mixing of ligand π-orbitals and cobalt d-orbitals in the planar conjugate chelate rings. The redox behaviour of the complexes of above chelates,with cobalt in the formal oxidation states Co(III), Co(II) and Co(I) as well as the chemical and photochemical reactions at the cobalt-axial ligand bond pointed out[1,6,7] strong similarities with the complexes of Vit.B_{12} group.

On the other hand some properties of the Vit.B_{12} coenzyme[5] were still lacking in the assumed model complexes: e.g. the positive charge of the complex ion (organometallic cation) and the solubility in water.

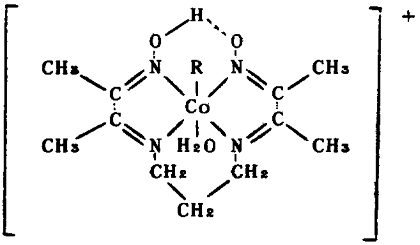


We succeeded in the preparation of novel organo-cobalt complexes having both the above requirements by adopting bis(diacetylmonoxime-imino)-propane 1,3=$(DOH)_2pn$ as tetradentate ligand.

This ligand was first prepared to obtain the complexes Ni$\{(DOH)(DO)pn\}X$ (X=ClO_4, Br, I, SCN)[9]. The perchlorate is supposed to have a square planar structure with ionically bound anion, while the other anions are coordinated to the nickel atom forming probably tetragonal pyramidal configurations.

When CoX_2 (X=Cl, Br, I) is reacted with $(DOH)_2pn$ in water-ethanol or water-acetone at room temperature, green crystalline complexes are obtained which correctly analyse for $[Co(III)\{(DOH)(DO)pn\}X_2]$ (I). The complexes are diamagnetic, soluble in alcohol, acetone, CH_2Cl_2 but insoluble in water. By reaction with NH_3, water soluble diamagnetic complexes are formed. Analyses and molar conductivity are in agreement with the formulas $[Co(III)\{(DOH)(DO)pn\}L_2]X_2$ when X=Br (II) and I (III) ($\Lambda_{II}=223$, $\Lambda_{III}=232$ ohm^{-1}cm^{2}). With aqueous $NaClO_4$ both (II) and (III) give $[Co(III)\{(DOH)(DO)pn\}L_2](ClO_4)_2$ ($\Lambda = 227$ ohm^{-1}cm^{2}).

Organometallic derivatives are obtained by reaction of (I) (X=Br) with appropriate Grignard reagent in tetrahydrofurane. After hydrolysis of the reaction mixture, crystalline, orange-yellow complexes are precipitated with aqueous $NaClO_4$. Analytical results are correct for $[RCo(III)\{(DOH)(DO)pn\}H_2O]ClO_4$ (IV) (R=CH_3, C_2H_5).



With conc. aqueous KI the complexes $[RCo\{(DOH)(DO)pn\}I]$ (V) are obtained from the Grignard reaction mixture. The complexes (IV) and (V) are diamagnetic and soluble in water ($\Lambda_{IV} = 86\ ohm^{-1}cm^{2}$).

Electrophoresis confirms the presence of the organocobalt complex cation.

By treatment with $NaB(C_6H_5)_4$ the orange-yellow insoluble salts $[RCo\{(DOH)(DO)pn\}H_2O]\ B(C_6H_5)_4$ are precipitated from aqueous solutions of (IV) and (V).

The above organometallic complexes are obtained also by reduction of the complexes (I) with $NaBH_4$ in the presence of the appropriate alkyl halide. The intermediate formation of a Co(I) derivative is assumed by analogy with the parallel reaction of the cobaloximes[1] and of the Co(III)bis(acetylacetone)ethylendiamine and Co(III)bis(salicylaldehyde)-ethylendiamine complexes.[6,7].

Stereochemistry of the present complexes is being studied by X ray investigations.

Complexes (IV) and (V) are the first examples of stable water soluble organocobalt compounds besides Vit.B_{12} coenzyme and the alkylcobalamins.

References

1. G.N.Schrauzer and J.Kohnle, Chem.Ber. 97, 3056 (1964)
   G.N.Schrauzer,R.J.Windgassen and J.Kohnle, ibid.98, 3324 (1965)
   G.N.Schrauzer and R.J.Windgassen, ibid. 99, 602 (1966)
   G.N.Schrauzer and R.J.Windgassen, J.Am.Chem.Soc. 88, 3738 (1966).
2. G.Costa, G.Mestroni,G.Tauzher and L.Stefani, J.Organometal.Chem. 6,181 (1966).
3. G.Costa,G.Mestroni and L.Stefani, J.Organometal.Chem. 7, 493 (1967).
4. E.Frasson, C.Panattoni and coll., Acta Cryst. 12, 201, 1027 (1959); 13, 893 (1960)
   K.S.Viswanathan and R.N.Kunchur, ibid. 14, 675 (1961).
5. A.E.Martell and R.Calvin, "Chemistry of the Metal Chelate Compounds", Prentice Hall, Englewood Cliffs, N.J., 4th Ed., 1959, p.266.
6. G.Costa and G.Mestroni, Tetrahedron Letters 19, 1783 (1967).
7. G.Costa and G.Mestroni, Tetrahedron Letters 19, 1781 (1967).
8. R.Bonnet, Chem.Rev.63, 573 (1963).
9. E.Uhlig and M.Friedrich, Z.Anorg.Allgem.Chem. 343, 229 (1966).