BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2552—2555 (1969)

The Syntheses and the Structure of Triethanolamine Complexes with Cobalt(II) and Nickel(II)[1]

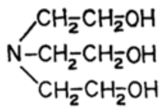
Yoshio KUGE[*1] and Shoichiro YAMADA

Institute of Chemistry, College of General Education, Osaka University, Toyonaka-shi, Osaka

(Received March 18, 1969)

Triethanolamine complexes with cobalt(II) and nickel(II) have been synthesized as crystals and examined on the basis of analytical data, electronic absorption spectra, and magnetic moments. A complex, $Ni\{N(CH_2CH_2OH)_3\}(ClO_4)_2$, which is formed with $Ni(ClO_4)_2$, is concluded to have a six-coordinated configuration, similar to that previously reported for the corresponding chloride, bromide, and nitrate complexes. In cobalt(II) complexes, $Co\{N(CH_2CH_2OH)_2(CH_2CH_2O)\}X$, which are formed with CoX_2 ($X=Cl^-$, Br^-, or NCS^-), the cobalt(II) ion is concluded to take a five-coordinated configuration.

A number of papers have been published concerning the behavior of metal complexes with triethanolamine (Formula I) in solution, but little is known about these complexes in the solid state.[2-4]



Formula I

Examining these complexes in the solid state by magnetic, spectroscopic, and X-ray powder techniques, Hughes and Rutt[5] recently reached some significant conclusions about their stoichiometry and stereochemistry. Independently, the present authors have also carried out a similar study of this subject. Many of our conclusions agree with the conclusions of the earlier reports, but our study has also yielded some conclusions which are different from those in the previous works, or which seem to be of a more conclusive nature than those of the previous papers. Moreover, among the previous workers there has been some disagreement event about the stoichiometry of the solid compounds. The present paper is concerned with the syntheses and the structures of the triethanolamine complexes with cobalt(II) and nickel(II), but emphasis will be placed upon the new and more significant results and on those of our conclusions which are different from those of the previous papers.

Experimental

Materials. Since the composition of the solid complexes reported in the present paper markedly depends upon the precise conditions of preparation, it seems wise to give here a detailed account of the preparation.

Cobalt(II) complexes of triethanolamine were prepared as purple crystals in the following manner. Into a solution of $CoX_2\cdot 6H_2O$ ($X=Cl^-$, Br^-, or NCS^-) (0.0125 mol) in 95% ethanol (100 m*l*), triethanolamine (0.025 mol) was stirred at room temperature. Purple crystals immediately began to separate out in the solution. After the solution had been stirred for about 30 min, the purple crystals of $Co\{N(CH_2CH_2OH)_2(CH_2CH_2O)\}X$ were collected by filtration, washed with cold ethanol, and dried overnight in a vacuum desiccator.

The solubility of these complexes in solvents like water, methanol and ethanol is quite low.

Employing a method essentially the same as that described above, Duff and Steer[4] obtained crystals of the same compositions as ours, but Hughes and Rutt[5] reported compounds with the $[Co\{N(CH_2CH_2OH)_3\}_2]X_2$ formula.

Nickel(II) complexes of triethanolamine of the $[Ni\{N(CH_2CH_2OH)_3\}_2]X_2$ formula ($X=Cl^-$, Br^-, NO_3^-, or ClO_4^-), were prepared as pale-blue crystals in the present work. The former three ($X=Cl^-$, Br^-, or NO_3^-) had been reported previously,[2,3,5] but the complex with $X=ClO_4^-$ had not been.

The method in the present work was as follows. Into a solution of $NiX_2.6H_2O$ ($X=Cl^-$, Br^-, NO_3^-, or ClO_4^-) (0.025 mol) in 95% ethanol (100 m*l*), we stirred triethanolamine (0.055 mol) in small portions at about 60°C. After being kept at this temperature

---

[*1] Present address: Osaka Public Health Institute, Mori-machi, Higashi-ku, Osaka.

[1] Presented, in part, at the 17th Symposium on Coordination Chemistry, Hiroshima, December, 1967.

[2] W. Hieber and E. Levy, *Z. anorg. Chem.*, **219**, 225 (1934).

[3] H. Tettamanzi and B. Carli, *Gazzetta Chim. Ital.*, **63**, 566 (1933); *ibid.*, **64**, 315 (1934).

[4] J. C. Duff and E. H. Steer, *J. Chem. Soc.*, **1932**, 2861.

[5] M. N. Hughes and K. J. Rutt, *J. Chem. Soc.*, *A*, **1968**, 2788.

TABLE 1. ANALYTICAL DATA OF COBALT (II) AND NICKEL (II) COMPLEXES OF TRIETHANOLAMINE

Compound		C(%)	H(%)	N(%)	Metal	halogen	μ*
$[Ni\{N(CH_2CH_2OH)_3\}_2](ClO_4)_2$	Found	25.47	5.23	5.14	10.20	—	3.05
	Calcd	25.92	5.44	5.04	10.55	—	
Co(TEA′)Cl**	Found	30.13	6.05	6.09	23.80	14.18	4.35
	Calcd	29.73	5.82	5.77	24.29	14.61	
Co(TEA′)Br	Found	25.25	4.77	4.89	20.14	27.74	4.30
	Calcd	25.11	4.57	4.88	20.53	27.84	
Co(TEA′)NCS	Found	31.06	5.46	10.45	21.67	—	4.38
	Calcd	31.71	5.32	10.56	22.22	—	

* μ: magnetic moment at room temperature in B. M.

** The notaiton, TEA′, represents an anionic ligand, $N(CH_2CH_2OH)_2(CH_2CH_2O)$.

for about 30 min, the solution was allowed to stand overnight at room temperature. A pale-blue precipitate which was formed in the solution was recrystallized from methanol. Pale-blue crystals of $[Ni\{N(CH_2CH_2OH)_3\}_2]X_2$ were thus obtained.

These complexes with $X=Cl^-$, Br^-, or NO_3^- are slightly soluble in methanol, but are almost insoluble in other solvents. The complex with $X=ClO_4^-$ is more soluble in methanol than are the othet three complexes.

With $X=ClO_4^-$, Hughes and Rutt⁵⁾ isolated a solid complex with a complicated formula.

Elemental analyses of those cobalt(II) and nickel(II) complexes whose composition remains still in dispute are given in Table 1.

Measurements. The electronic absorption spectra of the complexes in the solid state were determined with a Shimadzu QR-50 and a Shimadzu MPS-50L spectrophotometer. The measurement of the solution spectrum was possible only with $[Ni\{N(CH_2CH_2OH)_3\}_2](ClO_4)_2$. The solubilities of the other complexes in suitable solvents were too low for any accurate determination of the solution spectrum.

The X-ray diffraction diagrams were obtained with a Toshiba ADX-103 X-ray diffractometer.

The magnetic moments of the complexes were determined by the Gouy method at room temperature.

Results and Discussion

It was previously concluded, from the electronic spectra,⁵⁾ that the nickel(II) complexes $[Ni\{N(CH_2CH_2OH)_3\}]X_2$ with $X=Cl,^-$ Br^-, or NO_3^- consisted of six-coordinated complex-ions.

The new complex, $[Ni\{N(CH_2CH_2OH)_3\}_2](ClO_4)_2$, in the solid state shows a spectrum which is quite similar to those of the corresponding complexes with $X=Cl^-$, Br^-, and NO_3^-, as is shown in Fig. 1. Since all these nickel(II) complexes in the solid state show absorption bands at nearly the same frequencies, they may be considered to take a quite similar configuration. The absorption bands at about 11.0, 16.7, and 26.5 kK may be assigned to $^3T_{2g}\leftarrow{}^3A_{2g}$, $^3T_{1g}(F)\leftarrow{}^3A_{2g}$, and $^3T_{1g}(P)\leftarrow{}^3A_{2g}$ in the scheme of the O_h-field symmetry. As has also been concluded previously,⁵⁾ it is most likely that triethanolamine normally acts as a terdentate ligand with one hydroxyl-group remaining uncoordianted, although this ligand is structurally related to β,β',β''-triaminotriethylamine, which can function as a quadridentate ligand.

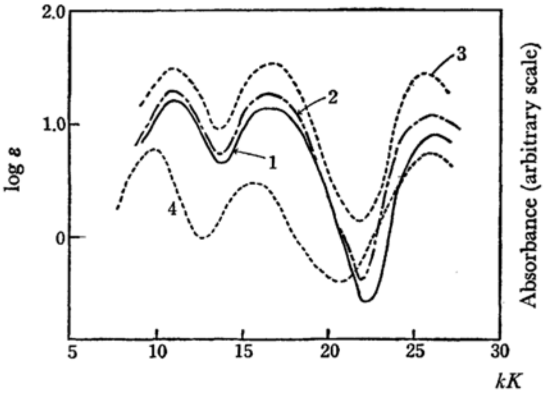


Fig. 1. Electronic absorption spectra of $[Ni\{N(CH_2CH_2OH)_3\}_2]X_2$.
1, $X=Br^-$, reflectance; 2, $X=NO_3^-$, reflectance; 3, $X=ClO_4^-$, reflectance; 4, $X=ClO_4^-$, in methanol. The scale on the right hand side refers to the curves 1, 2, and 3, and the scale on the left hand side the curve 4.

The absorption spectrum of $[Ni\{N(CH_2CH_2OH)_3\}_2](ClO_4)_2$ in methanol is found to be consistent with the octahedral configuration, but the band maxima in the solution spectrum are shifted toward much lower frequencies, indicating that the configuration of $[Ni\{N(CH_2CH_2OH)_3\}_2](ClO_4)_2$ in methanol may be considerably distorted compared with that in the solid state as well as with the regular octahedron.

The cobalt(II) complexes, $Co\{N(CH_2CH_2OH)_2(CH_2CH_2O)\}X$ ($X=Cl^-$, Br^-, and NCS^-), show quite similar spectra, as is shown in Fig. 2. It is found that these spectra cannot be consistently interpreted in terms of tetrahedral or an octahedral configuration.⁶⁾ Instead, they are similar to the

---

6) S. Buffagni and T. M. Dunn, *Nature*, **188**, 937 (1960); D. L. M. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 1161 (1961).

spectra of some cobalt(II) complexes of high-spin type, for which a five-coordinated structure has been established with certainty.7)

The magnetic moments of these cobalt(II) complexes, as shown in Table 1, seem to be too low for the six-coordinated cobalt(II) complexes, but they lie in a range which may reasonably be expected for the moments of the five-coordinated cobalt(II) complexes with ligands of this kind.7) It may, therefore, be presumed that in the $\mathrm{Co\{N(CH_2CH_2OH)_2(CH_2CH_2O)\}X}$ complexes ($\mathrm{X=Cl^-}$, $\mathrm{Br^-}$, or $\mathrm{NCS^-}$), the cobalt(II) ion takes a five-coordinated configuration.

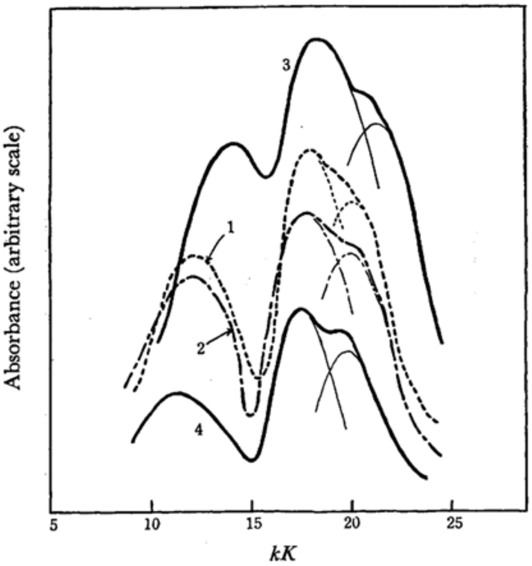
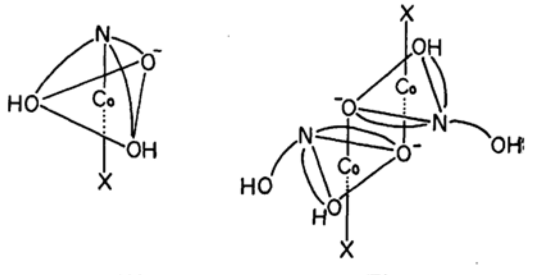


Fig. 2. Electronic absorption spectra of $\mathrm{Co\{N(CH_2CH_2OH)_2(CH_2CH_2O)\}X}$ (compound I) and $\mathrm{[Co(Me_4daeo)NCS]NCS}$ (compound II) in the solid state. The notation $\mathrm{Me_4daeo}$ denotes a molecule of $\mathrm{O\{CH_2CH_2N(CH_3)_2\}_2}$.
1, compound I, $\mathrm{X=Cl^-}$; 2, compound I, $\mathrm{X=Br^-}$; 3, compound I, $\mathrm{X=NCS^-}$; 4, compound II. The curve 4 is taken from Ref. 7 in the text.

The close similarity of the spectra of these cobalt(II) complexes seems to indicate that they have a similar configuration, one in which the cobalt(II) ions take five-coordination. In agreement with this may be the fact that the X-ray powder diagram of $\mathrm{Co\{N(CH_2CH_2OH)_2(CH_2CH_2O)\}Cl}$ has been found in the present work to be quite similar to that of the bromide analogue.*2

For the configuration of the five-coordinated cobalt(II) complexes, the (A) configuration in Fig. 3 might at first sight be considered to be possible. This configuration, however, seems to be unlikely, since it is more likely that the ligand, $\mathrm{N(CH_2CH_2OH)_2(CH_2CH_2O)}$, is a terdentate rather than a quadridentate ligand, judging from the findings on the corresponding nickel(II) complexes. The presence of one negatively-charged alcoholate group in the ligand suggests that these cobalt(II) complexes are binuclear or polynuclear, with bridging oxygen in the alcoholate group and with the chloride ion also coordinated to the cobalt(II) ion. The binuclear structure (B) in Fig. 3, like that found for the cobalt(II) complex with *N*-methylsalicylideneiminate,8) may be considered to be one of the most probable for the present cobalt(II) complexes. Any final conclusion about the precise configuration must, however, await further studies, based, for example, upon the X-ray crystal analysis.



(A) (B)

Fig. 3. Some possible configurations of $\mathrm{Co\{N(CH_2CH_2OH)_2(CH_2CH_2O)\}X}$, in which the cobalt(II) ion takes a five-coordination.

It should be noted that a difference is observed between the cobalt(II) and the nickel(II) ion in the stereochemistry of their triethanolamine complexes. This difference seems to be in agreement with previous studies showing that the stability of the five-coordinated configuration *vis-à-vis* the six-coordinated configuration is higher for the cobalt(II) than for the nickel(II) ion.9)

It is also interesting to compare the triethanolamine complexes with the corresponding complexes of $\mathrm{N\{CH_2CH_2N(C_2H_5)_2\}_3}$. The present work reveals that $\mathrm{NiX_2}$ ($\mathrm{X=Cl^-}$, $\mathrm{Br^-}$, or $\mathrm{NO_3^-}$) forms six-coordinated complexes with the former ligand, while it has previously been shown7) that five-coordinated complexes are formed with the latter ligand. The former and the latter ligands are found to function as terdentate and quadridentate

---

7) M. Ciampolini, N. Nardi and G. P. Speroni, *Coordin. Chem. Rev.*, **1**, 222 (1966); M. Ciampolini and N. Nardi, *Inorg. Chem.*, **6**, 445 (1967); *ibid.*, **5**, 1150 (1966).

[*2] The low solubility of these complexes in suitable solvents did not allow any accurate determination of the conductivity or the molecular weight.

8) P. L. Orioli, M. Di Vaira and L. Sacconi, *Chem. Commun.*, **1965**, 103; *Inorg. Chem.*, **5**, 400 (1966).

9) S. Yamada, E. Ohno, Y. Kuge, A. Takeuchi, K. Yamanouchi and K. Iwasaki, *Coordin. Chem. Rev.*, **3**, 247 (1968); S. Yamada, A. Takeuchi, K. Yamanouchi and K. Iwasaki, This Bulletin, **42**, 131 (1969).

ligands, respectively. The difference between the two ligands lies only in the terminal groups, the ability of the OH-group to combine with the metal ion being considered to be lower than that of the NR_2-group.

The present authors wish to thank the Ministry of Education for its financial support.