September, 1983] © *1983 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***56***, *2843—2844 (1983)* 2843

Halogenation of Mixed Ligand Cobalt(III) Complexes with 12- or 13-Membered Tetraaza Macrocycle and Acetylacetone, $[Co[Z]aneN_4(acac)](ClO_4)_2$ (Z=12, 13)

Akira Hirano, Naohide Matsumoto,* and Akira Ohyoshi
Department of Industrial Chemistry Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860

(Received March 11, 1983)

Synopsis. The parent cobalt(III) complex $[Co[12]aneN_4(acac)](ClO_4)_2$, $[Co[12]aneN_4(bzac)](ClO_4)_2$, or $[Co[13]aneN_4(acac)](ClO_4)_2$ reacts with *N*-halogenosuccinimide to give the substituted complex $[Co[12]aneN_4(Xacac)](ClO_4)_2$, $[Co[12]aneN_4(Xbzac)](ClO_4)_2$, or $[Co[13]aneN_4(Xacac)](ClO_4)_2$, where $[12]aneN_4$=1,4,7,10-tetraazacyclododecane, $[13]aneN_4$=1,4,7,10-tetraazacyclotridecane, acac=acetylacetonato, bzac=benzoylacetonato, X=Cl, Br.

Kuroda and coworkers[1,2] have studied the halogenation and nitration of $[CoA_4(acac)]^{2+}$ and succeeded to prepare the halogenated and nitrated complexes $[CoA_4(Xacac)]^{2+}$, where $A_4=(NH_3)_4$, (ethylenediamine)$_2$, 3,6-diazaoctane-1,8-diamine. Previously we reported the synthesis, spectral characterization, and X-ray analysis of $[Co[12]aneN_4(acac)](ClO_4)_2$ and its brominated complex $[Co[12]aneN_4(Bracac)](ClO_4)_2$, in which the cobalt ion is coordinated in a distorted octahedral fashion to four nitrogen atoms of $[12]aneN_4$ and two oxygen atoms of the acetylacetonato moiety in a cis position.[3] As an extension of the study, we wish to report the synthesis and spectral characterization of the halogenated complexes $[Co[Z]aneN_4(Xacac)](ClO_4)_2$ and $[Co[12]aneN_4(Xbzac)](ClO_4)_2$ (Z=12, 13; X=Cl, Br).

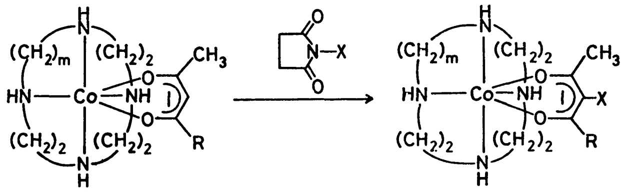

Fig. 1. Synthetic scheme and abbreviations of complexes $[Co[Z]aneN_4(Xacac)]^{2+}$: Z=12 (m=2), Z=13 (m=3), X=H, C, Br, R=CH_3; $[Co[12]aneN_4(Xbzac)]^{2+}$: X=H, Cl, Br, R=$C_6H_5$.

Experimental

Measurements. Infrared spectra were recorded as KBr disks on a Shimadzu IR-410, while visible and ultraviolet spectra were measured in aqueous solutions on a Hitachi recording spectrophotometer 323. Conductivity measurements were carried out by a Denki Kagaku AOC-10 at *ca.* 10^{-3} mol dm^{-3} in aqueous solutions at room temperature. The 100 MHz ^1H NMR spectra were recorded by a JEOL MH 100 spectrometer at room temperature. The solvent used was deuterium oxide and shift measurements were made relative to 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt.

Syntheses. The macrocyclic ligands, 1,4,7,10-tetraazacyclododecane ($[12]aneN_4$) and 1,4,7,10-tetraazacyclotridecane ($[13]aneN_4$) were prepared according to the high yield synthetic method of Raymond *et al.*[4] which was applied for the synthesis of $[16]aneN_4$. The unsubstituted (parent) complexes $[Co[12]aneN_4(acac)](ClO_4)_2$ and $[Co[12]aneN_4(bzac)](ClO_4)_2$ were prepared by the reaction of $[Co[12]aneN_4CO_3]ClO_4$ and acetylacetone or benzoylacetone according to a similar method described previously.[3] The complex $[Co[13]aneN_4(acac)](ClO_4)_2$ was prepared by the reaction of cis/trans mixture of $[Co[13]aneN_4Cl_2]ClO_4$[5] and acetylacetone. To a solution of 2.0 g of cis/trans mixture of $[Co[13]aneN_4Cl_2]ClO_4$ in 10 cm^3 of water is added a solution of 1.5 cm^3 of acetylacetone in 10 cm^3 of 1 M NaOH. The solution was stirred at *ca.* 50 °C for 2 h. After the addition of several drops of 6 M $HClO_4$, the solution was left at room temperature to precipitate red crystals. They were collected and recrystallized from a dilute $HClO_4$ solution. The substituted complexes $[Co[Z]aneN_4(Xacac)](ClO_4)_2$ and $[Co[12]aneN_4(Xbzac)](ClO_4)_2$ (Z=12, 13; X=Cl, Br) were prepared according to a similar method of Kuroda *et al.* which was used for the preparation of $[CoA_4(Xacac)](ClO_4)_2$.[1,2]

Results and Discussion

The elemental analytical data for C, H, and N, along with the molar electrical conductances are given in Table 1. The molar electrical conductances are in the range of 197—236 S cm^2 mol^{-1} and these values are in the expected range for the 1:2 electrolytes,[6] and consistent with the formula of $[Co[Z]aneN_4(Xacac)]^{2+}$.

Spectral data of infrared, ^1H NMR, and electronic spectra are summerized in Table 2. The infrared spectra of unsubstituted complexes exhibit two strong bands in the region of 1500—1600 cm^{-1}, which are assignable to ν(C=O) and ν(C=C). On the other hand, the substituted complexes have only one band in the region. This spectral feature has been found in the well-characterized complexes such as $[M(Xacac)_3]$ (M=Cr^{3+}, Co^{3+}; X=H, Cl, Br, I),[7] providing an evidence of the substitution. Busch *et al.*[5] have shown that the infrared bands in the CH_2 rocking region (800—910 cm^{-1}) can be used to distinguish cis from trans isomers of $[Co[13—16]aneN_4CO_3]^+$. The infrared spectra of the present complexes $[Co[13]aneN_4(Xacac)](ClO_4)_2$ (X=H, Cl, Br) are in accord with the formation of the cis complexes.

The ^1H NMR spectra were measured to verify the substitution on the γ-carbon of the acetylacetonato residue. The methine proton resonance about 6.5 ppm of the unsubstituted complexes disappeared in the halogenated complexes, providing further evidence of the substitution on the γ-position. The methyl proton resonance around 2.3 ppm of the unsubstituted complexes shifted to lower magnetic field upon the substitution.

Some of the electronic spectra are shown in Fig. 2. Electronic spectra are quite similar to each other

Table 1. Elemental analytical data for C, H, and N, along with the molar electrical conductances

	Complex	C (%) Found (Calcd)	H (%) Found (Calcd)	N (%) Found (Calcd)	Conductance S^{-1} mol^{-1} cm^2
1	[Co[12]aneN$_4$(Clacac)](ClO$_4$)$_2\cdot$H$_2$O	26.51 (26.84)	4.59 (4.84)	9.74 (9.63)	236
2	[Co[12]aneN$_4$(bzac)](ClO$_4$)$_2$	36.36 (36.56)	4.92 (4.94)	9.54 (9.47)	197
3	[Co[12]aneN$_4$(Clbzac)](ClO$_4$)$_2\cdot$0.5H$_2$O	34.06 (34.00)	4.56 (4.45)	8.80 (8.83)	217
4	[Co[12]aneN$_4$(Brbzac)](ClO$_4$)$_2\cdot$0.5H$_2$O	31.83 (31.83)	4.28 (4.30)	8.26 (8.25)	217
5	[Co[13]aneN$_4$(acac)](ClO$_4$)$_2\cdot$0.5H$_2$O	30.50 (30.45)	5.50 (5.48)	10.35 (10.15)	206
6	[Co[13]aneN$_4$(Clacac)](ClO$_4$)$_2$	29.14 (29.11)	4.86 (4.89)	9.81 (9.70)	204
7	[Co[13]aneN$_4$(Bracac)](ClO$_4$)$_2$	27.11 (27.03)	4.51 (4.54)	9.08 (9.01)	206

Table 2. Spectral data of infrared, ^{1}H NMR, and electronic spectra

	ν(C$\overset{\cdots}{-}$O, C$\overset{\cdots}{-}$C) cm^{-1}	Methine (ppm)	Methyl (ppm)	First band of d-d $\tilde{\nu}/10^3$ cm^{-1} (ε)	Specific band $\tilde{\nu}/10^3$ cm^{-1} (ε)	Dq^{av} a) cm^{-1}
1	1558	—	2.54, 2.57	18.7 (310)	28.8 (3200)	2250
2	1558, 1515	6.57	2.34	18.7 (340)	28.1 (6800)	2250
3	1543	—	2.72	18.8 (340)	27.8 (4400)	2260
4	1549	—	2.66	18.7 (350)	27.5 (4700)	2250
5	1570, 1524	6.36	2.21	19.8 (240)	30.5 (3400)	2360
6	1556	—	2.46	19.7 (240)	29.0 (3500)	2350
7	1557	—	2.56	19.7 (270)	29.0 (3300)	2350

a) Evaluated by $10Dq^{\mathrm{av}} = \nu^1\mathrm{T}_{1\mathrm{g}} \leftarrow {}^1\mathrm{A}_{1\mathrm{g}} + 3800.$[5)]

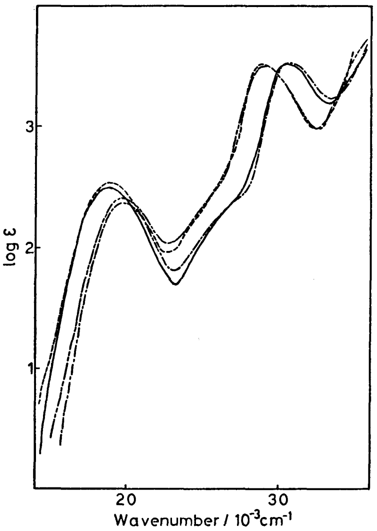

Fig. 2. Electronic spectra of [Co[12]aneN$_4$(acac)](ClO$_4$)$_2\cdot$H$_2$O (——), [Co[12]aneN$_4$(Bracac)](ClO$_4$)$_2\cdot$0.5H$_2$O (······), [Co[13]aneN$_4$(acac)](ClO$_4$)$_2\cdot$0.5H$_2$O (—·—), and [Co[13]aneN$_4$(Bracac)](ClO$_4$)$_2$ (—··—).

and to the related low-spin six-coordinated cobalt(III) complexes, such as [CoA$_4$(Xacac)]$^{2+}$.[1,2)] The spectra exhibit two bands attributable to the d-d transitions, $^1\mathrm{T}_{1\mathrm{g}} \leftarrow {}^1\mathrm{A}_{1\mathrm{g}}$ and $^1\mathrm{T}_{2\mathrm{g}} \leftarrow {}^1\mathrm{A}_{1\mathrm{g}}$, in which the latter band appeared as shoulder. The average ligand field strength Dq^{av} can be evaluated to be 2250 and 2350 cm^{-1} for the 12- and 13-membered complexes, respectively. The data indicated that the ligand [13]aneN$_4$ provides a stronger ligand field than [12]aneN$_4$ does, being consistent with the result of [Co[12—13]aneN$_4$CO$_3$]$^+$.[5)] The spectra exhibit also a specific band attributable to the charge-transfer band from metal t$_{2\mathrm{g}}$ to ligand π^* orbital.[8)] The specific band shifted to lower wave number upon the substitution, while the d-d transitions showed no shift.

References

1) K. Kuroda and Y. Kamiiba, *Chem. Lett.*, **1975**, 1027.

2) K. Kuroda, K. Yoshitani, K. Kunigida, Y. Kamiiba, and K. Watanabe, *Bull. Chem. Soc. Jpn.*, **49**, 2445 (1976).

3) N. Matsumoto, A. Hirano, T. Hara, and A. Ohyoshi, *J. Chem. Soc., Dalton Trans.*, in press.

4) W. L. Smith, J. P. Ekstrand, and K. N. Raymond, *J. Am. Chem. Soc.*, **100**, 3539 (1978).

5) Y. Hung, L. Y. Martin, S. C. Jackels, A. M. Tait, and D. H. Busch, *J. Am. Chem. Soc.*, **99**, 4029 (1977), and references therein.

6) R. G. Hayter, *J. Am. Chem. Soc.*, **84**, 3046 (1962).

7) J. P. Collman, R. A. Moss, H. Maltz, and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961).

8) I. Hanazaki, F. Hanazaki, and S. Nagakura, *J. Chem. Phys.*, **50**, 265 (1969).