of D_2O. The intramolecular hydrogen bonding discussed above is responsible for the downfield shift of the hydroxyl proton. Figure 6 shows the FT ^1H NMR spectrum of the V(V) complex. (The vanadium(IV) complex was oxidized to give a diamagnetic analogue.[12]) The upfield portion of the spectrum (not shown) contains peaks from the supporting electrolyte (TEAP). No band between 9 and 13 ppm that would integrate to 1 (relative to the azomethine proton peak) was observed. The flat, broad band at about 13 ppm is probably the hydroxyl proton of a trace of dissociated ligand. Although two peaks appear between 10 and 11 ppm, they are sharp, unlike the hydroxyl proton peaks, and their integrations are much smaller than 1. Their presence is probably due to artifacts of the electrolytic process. Neither the NMR spectrum of the ligand (Figure 5) nor the spectrum of the vanadium(V) complex (Figure 6) showed evidence of the SH proton. As with IR, such NMR signals are often not observed.

An attempt to synthesize a vanadyl complex with *N*-(2-mercaptoethyl)benzylideneamine (prepared from benzaldehyde and 2-aminoethanethiol) was unsuccessful. Since this ligand has only N and S donating atoms, this result suggests that N and S bonding is unlikely in the complex with ligand I.

Conclusion

The IR studies, in both KBr and C_4Cl_6, give conclusive evidence that the hydroxyl group is involved in bonding to the vanadyl group in bis[*N*-(2-mercaptoethyl)salicylidineaminato]oxovanadium(IV). The NMR data support this. Thus, although the protonated SH group cannot be confirmed by either IR or NMR, we are convinced that the complex bonds through N and O donors. We are now attempting to grow suitable crystals for an X-ray structure determination of this complex.

Acknowledgment. Financial support for this work was provided by a Sigma Xi grant to R.S. and by the Research Corp. We also wish to acknowledge preliminary work on this project by S. L. Bernard and assistance in obtaining the FT NMR data by J. F. Sebastian.

Registry No. Bis[*N*-(2-mercaptoethyl)salicylidineaminato]oxovanadium(IV), 68433-47-6.

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[12] The NMR spectrum of the vanadium(IV) complex was recorded, but as expected, paramagnetic broadening obliterated the spectrum.

Contribution from the Departments of Chemistry,
University of Oklahoma, Norman, Oklahoma 73019,
Bowling Green State University, Bowling Green, Ohio 42403,
and University of Cincinnati, Cincinnati, Ohio 45221

Synthesis of $[Co(CoL_3)_2]^{3+}$ by HNO_3 Oxidation of CoL_3 (L = $^-SCH_2CH_2NH_2$) and Induced Electron Transfer. Crystal Structure of $[Co(CoL_3)_2]_2(SO_4)Cl_4$

Mary Jane Heeg,[1] E. L. Blinn,[2] and Edward Deutsch*[3]

Received August 8, 1984

The mechanisms governing oxidation of coordinated sulfur are diverse, and this diversity is of considerable relevance to catalytic and biological systems.[4] At least six different pathways exist for the oxidation of thiols coordinated to cobalt(III), and each of these paths leads to distinct reaction products. The mechanistic aspects of these systems have recently been reviewed.[4] In this context our observation that the HNO_3 oxidation of CoL_3 (where L represents $^-SCH_2CH_2NH_2$) leads to a product which can be formulated as "$CoL_2(NO_3)$" is of considerable interest. Since any mechanistic interpretation of this observation requires definitive knowledge of the identity of the "$CoL_2(NO_3)$" product, a single-crystal X-ray structural analysis of this material was undertaken. This paper presents the results of this analysis, which show that the "$CoL_2(NO_3)$" product is in fact the nitrate salt of the known trimeric complex $[Co(CoL_3)_2]^{3+}$.

The structure of the trimeric $[Co(CoL_3)_2]^{3+}$ complex is of interest in itself since it is dependent upon the ability of coordinated thiols to bridge metal centers. The single thiolato group of $[(en)_2CoL]^{2+}$ has been shown to effectively bridge the Co(III) center to Ag(I), Hg(II), Pt(II), Cu(I), and the iodonium ion.[5-7] While it has long been assumed that the bridging ability of coordinated thiols allows the facial isomer of CoL_3 to function as a tridentate, S-donating ligand to a variety of metal centers (Co(III), Ni(II), Fe(III), Ru(III), Zn(II), Cu(I), Cu(II), and Pb(II)),[8-12] none of these $[M(CoL_3)_n]^{m+}$adducts have been structurally characterized. The structural analysis presented in this work confirms the two tris(thiolato) bridges originating from the two terminal cobalt(III) ions and the octahedral arrangement of six sulfur atoms about the central cobalt(III) ion. This latter feature is in contrast to the trigonal-prismatic geometry of the central cobalt(II) ion found in the oxygen analogue $[Co(Co(OCH_2CH_2NH_2)_3)_2]^{2+}$.[13]

Experimental Section

HNO_3 Oxidation of CoL_3. $Co(SCH_2CH_2NH_2)_3$ was prepared by a published procedure.[8] Four grams of this material was slurried in 200 mL of water, and 52.5 mL of 0.16 M HNO_3 was added with stirring. On gentle heating for 30 min this stirred suspension changed from green to red-brown. Filtration of the reaction mixture and concentration of the filtrate yielded 0.70 g of brown crystalline product. Anal. Calcd for $Co(SCH_2CH_2NH_2)_2NO_3{\cdot}H_2O$: C, 16.50; H, 4.86; N, 14.59. Found: C, 16.33; H, 4.80; N, 14.56. An aqueous solution of this material was adsorbed onto SP-C25 cation-exchange resin and then eluted as a single band with 0.5 M LiCl. Addition of an equal volume of saturated $(NH_4)_2SO_4$ solution to this eluent, followed by slow cooling, yielded dark, red-brown, single crystals suitable for X-ray structural analysis.

Structural Analysis. A single crystal of dimensions 0.19 × 0.20 × 0.20 mm was selected and mounted on a CAD-4 automated diffractometer equipped with Mo Kα radiation and a graphite monochromator. A total of 11 098 reflections were collected at ambient temperature in the sphere $2.5° \leq 2\theta \leq 50°$. After averaging, 10 799 unique reflections were obtained; of these 7315 were observed reflections with $I_o \geq 3\sigma(I)$. Least-squares calculations on 25 high-angle reflections yielded a triclinic cell of dimensions $a = 11.803$ (3) Å, $b = 17.227$ (8) Å, $c = 17.239$ (4) Å; $\alpha = 83.24$ (2)°, $\beta = 69.98$ (2)°, $\gamma = 69.99$ (3)°, and $V = 3095$ (2) Å^3. Other details of data collection were as follows: scan method, $\theta/2\theta$; scan rate, variable up to 45 s/scan; scan range, calculated by $0.80 + 0.20 \tan \theta$ with 25% extension on each side for backgrounds. Three intensity monitors were checked every 2 h of X-ray time, and they were observed to fluctuate randomly <2% over the entire data collection. Three orientation standards were centered after every 200 observations. Absorption corrections were applied with μ(Mo Kα) = 22.2 cm^{-1}; transmission coefficients varied from 0.66 to 0.71. The calculated density was 1.615 g cm^{-3} with $Z = 4$.

The centrosymmetric space group[14] $P\bar{1}$ was assumed and gave satisfactory refinement. The Co and S atoms were placed according to a

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[1] University of Oklahoma.

[2] Bowling Green State University.

[3] University of Cincinnati.

[4] Deutsch, E.; Root, M. J.; Nosco, D. L. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 269-389.

[5] Heeg, M. J.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1979**, *18*, 2036-2039.

[6] Lane, R. H.; Pantaleo, N. S.; Farr, J. K.; Coney, W. M.; Newton, M. G. *J. Am. Chem. Soc.* **1978**, *100*, 1610-1611.

[7] Nosco, D. L.; Heeg, M. J.; Glick, M. D.; Elder, R. C.; Deutsch, E. *J. Am. Chem. Soc.* **1980**, *102*, 7784-7786.

[8] Busch, D. H.; Jicha, D. C. *Inorg. Chem.* **1962**, *1*, 884-887.

[9] Freeh, G.; Chapman, K. M.; Blinn, E. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 91-94.

[10] DeSimone, R.; Ontko, R.; Wardman, L.; Blinn, E. L. *Inorg. Chem.* **1975**, *14*, 1313-1316.

[11] Blinn, E. L.; Butler, P.; Chapman, K. M.; Harris, S. *Inorg. Chim. Acta* **1977**, *24*, 139-143.

[12] Butler, P. R.; Blinn, E. L. *Inorg. Chem.* **1978**, *17*, 2037-2039.

[13] Bertrand, J. A.; Kelly, J. A.; Vassian, E. G. *J. Am. Chem. Soc.* **1969**, *91*, 2394-2395.

[14] "International Tables for X-ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1969; Vol. 1.

0020-1669/85/1324-1118$01.50/0

Table I. Final Atomic Positional Parameters for Non-Hydrogen Atoms in $[Co(CoL_3)_2]_2(SO_4)Cl_4$, L = $^-SCH_2CH_2NH_2$[a]

atom	*x*	*y*	*z*
Co1	0.44505 (9)	−0.09929 (6)	0.40522 (6)
Co2	0.50000	0.0	0.50000
Co3	0.15429 (9)	0.59485 (6)	0.40067 (6)
Co4	0.0	0.50000	0.50000
Co5	0.14973 (9)	−0.09478 (6)	0.09939 (6)
Co6	0.0	0.0	0.0
Co7	0.24904 (9)	0.40067 (5)	−0.09478 (6)
Co8	0.0	0.50000	0.0
S1	0.4874 (2)	0.0191 (1)	0.3713 (1)
S2	0.6001 (2)	−0.1338 (1)	0.4620 (1)
S3	0.3215 (2)	−0.0352 (1)	0.5261 (1)
S4	−0.0066 (2)	0.6287 (1)	0.5191 (1)
S5	0.0337 (2)	0.5381 (1)	0.3662 (1)
S6	0.2138 (2)	0.4740 (1)	0.4649 (1)
S7	0.1411 (2)	−0.1287 (1)	−0.0191 (1)
S8	−0.0622 (2)	−0.0381 (1)	0.1338 (1)
S9	0.1525 (2)	0.0261 (1)	0.0352 (1)
S10	0.1221 (2)	0.5192 (1)	−0.1287 (1)
S11	0.0717 (2)	0.3662 (1)	−0.0382 (1)
S12	0.1878 (2)	0.4648 (1)	0.0261 (1)
S13	0.3750 (2)	0.7499 (1)	0.2500 (1)
Cl1	0.1248 (2)	0.2502 (1)	0.7500 (1)
Cl2	0.3104 (4)	0.0640 (2)	0.1981 (2)
Cl3	0.1256 (3)	0.8017 (2)	0.5643 (2)
Cl4	0.4273 (3)	0.5642 (2)	0.8979 (2)
Cl5	0.4914 (3)	0.6981 (2)	0.9358 (2)
O1	0.3558 (5)	0.6974 (3)	0.1969 (3)
O2	0.4465 (5)	0.8028 (3)	0.1974 (3)
O3	0.2504 (4)	0.8028 (3)	0.3028 (3)
O4	0.4468 (4)	0.6971 (3)	0.3027 (3)
N1	0.5677 (6)	−0.1431 (4)	0.2958 (4)
N2	0.4153 (6)	−0.2068 (4)	0.4468 (4)
N3	0.2934 (6)	−0.0581 (4)	0.3663 (4)
N4	0.0755 (6)	0.7042 (4)	0.3565 (4)
N5	0.2916 (6)	0.5537 (4)	0.2933 (4)
N6	0.2648 (6)	0.6335 (4)	0.4421 (4)
N7	0.1358 (6)	−0.2042 (4)	0.1434 (4)
N8	0.1390 (6)	−0.0538 (4)	0.2060 (4)
N9	0.3405 (6)	−0.1336 (4)	0.0580 (4)
N10	0.2790 (5)	0.3568 (4)	−0.2041 (4)
N11	0.3446 (6)	0.2939 (4)	−0.0536 (4)
N12	0.3984 (5)	0.4421 (4)	−0.1339 (4)
C1	0.6362 (8)	−0.0233 (5)	0.2887 (5)
C2	0.6130 (8)	−0.0806 (5)	0.2391 (5)
C3	0.5370 (8)	−0.2049 (5)	0.5371 (5)
C4	0.5074 (9)	−0.2607 (5)	0.4881 (6)
C5	0.1997 (7)	0.0361 (5)	0.4856 (6)
C6	0.1742 (7)	−0.0144 (5)	0.4311 (5)
C7	−0.1132 (7)	0.7108 (5)	0.4768 (5)
C8	−0.0330 (7)	0.7609 (5)	0.4195 (5)
C9	0.1680 (8)	0.4634 (5)	0.2946 (5)
C10	0.2524 (8)	0.5110 (6)	0.2397 (5)
C11	0.2642 (8)	0.5141 (5)	0.5359 (5)
C12	0.3403 (8)	0.5689 (6)	0.4861 (6)
C13	0.0744 (8)	−0.2109 (5)	0.0227 (5)
C14	0.1475 (7)	−0.2608 (5)	0.0804 (5)
C15	−0.0760 (7)	0.0366 (5)	0.2060 (5)
C16	0.0041 (8)	−0.0135 (6)	0.2611 (5)
C17	0.3150 (7)	−0.0139 (6)	−0.0366 (5)
C18	0.3949 (7)	−0.0691 (5)	0.0142 (5)
C19	0.0981 (8)	0.4770 (6)	−0.2111 (5)
C20	0.2286 (7)	0.4196 (5)	−0.2604 (5)
C21	0.1312 (7)	0.2946 (5)	0.0368 (5)
C22	0.2637 (8)	0.2404 (5)	−0.0113 (6)
C23	0.2791 (8)	0.5354 (5)	−0.0136 (5)
C24	0.4094 (7)	0.4861 (5)	−0.0690 (5)

[a] Estimated standard deviations in parentheses refer to the last digit.

Table II. Selected Interatomic Distances (Å) and Angles (deg) (Averaged)[a]

Co_t–S	2.238 (7)	S–C	1.821 (7)
Co_c–S	2.262 (11)	N–C	1.489 (14)
Co···Co	2.857 (1)	C–C	1.526 (12)
Co–N	1.996 (8)	S–O (anion)	1.476 (2)
Co_t–S–Co_c	78.8 (4)	C–C–N	109 (1)
S–Co_t–S	84.5 (8)	Co_t–N–C	113.8 (4)
N–Co_t–N	94.6 (6)	Co_c–S–C	114.8 (9)
S–Co_t–N	88.3 (2)	S–Co_c–S[b]	83.5 (9)
Co_t–S–C	95.6 (6)	O–S–O (anion)	109.5 (4)
S–C–C	106.4 (6)		

[a] Key: Co_t = Co(terminal); Co_c = Co(central). [b] This angle is given only for unique sulfur atoms, i.e. those not related by the inversion center at Co_c.

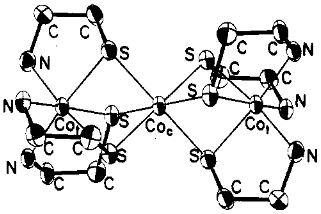

Figure 1. ORTEP drawing of the $[Co(CoL_3)_2]^{3+}$ cation. These particular atoms were drawn with use of the coordinates and thermal parameters for Co1 and Co2 and their ligands but are representative of the remaining independent cations since all the $[Co(CoL_3)_2]^{3+}$ cations are (noncrystallographically) equivalent.

direct-methods solution,[15] and successive Fourier and difference Fourier maps revealed the locations of the remaining atoms. Apparently there is some disorder in three of the four independent chloride anions; these three appear to be distributed in four different locations in the cell and are thus assigned site occupancy factors of 0.75 (these are Cl2–5).[16] Hydrogen atoms in the cations were placed in calculated positions (C,-N–H = 1.08 Å, tetrahedral geometry) and held invariant with $U(H)$ = 0.06 Å^2. Full-matrix least squares was used to refine positional and temperature parameters until the final cycles, at which point all non-hydrogen atoms were described anisotropically and blocked matrices were used. The final R values on all observed reflections were R = 0.045 and R_w = 0.064.[17] The maximum shift in any parameter in the last cycles was 0.02σ. In a final difference map, scattered residual election density up to 1.4 e Å^{-3} suggests some partial occupancy by solvent (water) molecules. Neutral-atom scattering factors and corrections for anomalous dispersion were obtained from ref 18. Final atomic positional parameters are found in Table I. The unit cell contains four independent half-molecules, such that the central cobalt in the trinuclear cluster occupies a crystallographic center of symmetry. All four cationic halves are chemically equivalent, and averaged distances and angles are presented in Table II. Complete bond distances and angles, along with hydrogen atom positional parameters, non-hydrogen atom thermal parameters, and calculated and observed structure factors, are available.[19] Figure 1 illustrates the molecular geometry.

Results and Discussion

The structure of the trinuclear cationic product is shown in Figure 1. This complex consists of three octahedrally coordinated cobalt(III) centers that are joined by two sets of triple bridges, each bridge consisting of a coordinated thiolato sulfur atom. Each trimeric cation thus possesses six asymmetric sulfur atoms. The absolute configurations about the terminal CoL_3 centers are $\Delta\lambda\lambda\lambda$ and its enantiomorph $\Lambda\delta\delta\delta$, which combine to form the meso conformer.[20]

The central cobalt atom is coordinated to two S_3 faces in a trigonally distorted octahedron. The trigonal distortion has the

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(15) All computations were performed with use of local modifications of the programs of SHELX-76: Sheldrick, G. M. University Chemical Laboratory, Cambridge, England, 1976.

(16) Setting the thermal parameters of Cl2–5 equal to that of Cl1 and refining the occupancy factor yielded a value of 0.70. Therefore, assigning the site occupancy as 0.75 seems reasonable.

(17) $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(18) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(19) Supplementary material.

(20) A discussion of optically active and meso forms of $Co(CoL_3)_2^{3+}$ is given in: Brubaker, G. R.; Douglas, B. E. *Inorg. Chem.* **19678** *6*, 1562–1566.

effect of lengthening the molecule along the C_3 axis, as evidenced by nonbonded S···S distances. The average S···S distance within a triangular face originating from one terminal cobalt atom is 3.01 (2) Å, while the average S···S cis distance between sulfur atoms on different triangular faces is 3.38 (3) Å. These distances would be equal in a perfect octahedron. In the terminal cobalt(III) coordination sphere, the S–$\mathrm{Co_t}$–N "bite" angles are normal, averaging 88.3 (2)°; cf. 88.8 (2)° in $[(\mathrm{en})_2\mathrm{CoL}]^{2+}$.[21] However, all S–$\mathrm{Co_t}$–S angles are acute (average 84.5 (8)°) and all N–$\mathrm{Co_t}$–N angles are obtuse (average 94.6 (6)°), indicating a compression of the S_3 face and concomitant expansion of the N_3 face. This permits a slightly greater Co···Co separation while maintaining optimal Co–S distances. Both of the distortions just described argue against any metal–metal bonding and indicate some repulsion at a Co···Co distance of 2.857 (1) Å. Distortions due to internuclear repulsions have beeen noted for another triply bridged Co(III) binuclear complex, $[(\mathrm{Co}(\mathrm{C_8H_{18}N_2S_2}))_2\mathrm{NO}]^+$, where the Co···Co separation is 2.770 (2) Å.[22]

The sulfur atoms are nearly equally bound to the terminal and central cobalt atoms. Bond distances average 2.238 (7) Å for $\mathrm{Co_t}$–S and 2.262 (11) Å for $\mathrm{Co_c}$–S. The difference between these two values is small (0.024 (13) Å) and is at the 2σ level of significance, but it is noteworthy that every $\mathrm{Co_c}$–S distance is larger than every $\mathrm{Co_t}$–S distance (of 12 independent observations for each distance in this structure). Stated another way, the *fac*-$\mathrm{S_3}$ plane is 0.037 Å (average) closer to $\mathrm{Co_t}$ than $\mathrm{Co_c}$ (1.410 vs. 1.447 Å).

A substantial and fascinating network of hydrogen bonds exists within the lattice. Every amine hydrogen atom is clearly involved in a hydrogen bond to either a chloride or a sulfate oxygen atom. Each sulfate oxygen atom participates in three separate hydrogen bonds, utilizing every available free electron pair in this anion. The average H···O(sulfate) distance is 1.91 (1) Å for 12 entries averaged. The pattern of hydrogen bonding to chloride is most interesting in light of the apparent disorder in the chloride distribution. The atom Cl1, which possesses a site occupancy factor of 1.0 and shows no disorder, is associated with four distinct ammine hydrogen atoms in hydrogen bonding. In contrast, the remaining four chloride sites (Cl2–5) have been assigned occupancy factors of 0.75 and these sites engage the remaining ammine hydrogen atom in bonds at two bonds per site. The requirement for hydrogen bonding throughout the lattice apparently causes three chloride ions to be randomly distributed among these four similar lattice sites. Among the 12 hydrogen bonds to chloride, the average Cl···H distance is 2.31 (6) Å.

The stoichiometry of the synthesis of $[\mathrm{Co}(\mathrm{CoL_3})_2]^{3+}$ from $\mathrm{CoL_3}$ requires the generation of the central cobalt atom from excess $\mathrm{CoL_3}$ at some point during the reaction sequence. The central cobalt atom is most reasonably derived from labile cobalt(II) since it is known[8] that under aerobic conditions mixtures of cobalt(II) and $\mathrm{CoL_3}$ readily yield $[\mathrm{Co}(\mathrm{CoL_3})_2]^{3+}$. Thus, the major mechanistic point to be resolved in the synthesis of $[\mathrm{Co}(\mathrm{CoL_3})_2]^{3+}$ from $\mathrm{CoL_3}$ concerns the origin of Co(II). How does $\mathrm{HNO_3}$ oxidation of $\mathrm{CoL_3}$ yield the labile Co(II) center necessary for the construction of $[\mathrm{Co}(\mathrm{CoL_3})_2]^{3+}$?

Oxidation of coordinated thiols can occur by one of several pathways, internal electron transfer (IET) being a particularly intriguing and relatively uncommon case.[4] When a thiol is coordinated to a potentially oxidizing center such as Co(III) or Ru(III), 1-equiv *oxidation* of the thiol can lead to net *reduction* of the metal center. This occurs by IET, the metal center providing the second equivalent of oxidizing power necessary to complete the net 2-equiv oxidation of the coordinated thiol.[4] Thus, the observation of $[\mathrm{Co}(\mathrm{CoL_3})_2]^{3+}$ as a product strongly implies that the $\mathrm{HNO_3}$ oxidation of $\mathrm{CoL_3}$ proceeds via IET. The major steps of the net process are summarized as

$$\mathrm{CoL_3 + HNO_3 + H^+ \rightarrow CoL_2(NH_2CH_2CH_2S\cdot)^+ + NO_2 + H_2O}$$

$$\mathrm{H^+ + CoL_2(NH_2CH_2CH_2S\cdot)^+ \xrightarrow{IET} Co(II) + L + (NH_2CH_2CH_2S-)_2}$$

$$\mathrm{Co(II) + 2CoL_3 \rightarrow Co^{II}(CoL_3)_2{}^{2+}}$$

$$\mathrm{Co^{II}(CoL_3)_2{}^{2+} + HNO_3 + H^+ \rightarrow Co^{III}(CoL_3)_2{}^{3+} + NO_2 + H_2O}$$

Oxidants other than $\mathrm{HNO_3}$ (e.g. Ce(IV) and V(V)) also convert $\mathrm{CoL_3}$ to $[\mathrm{Co}(\mathrm{CoL_3})_2]^{3+}$,[11] and even boiling $\mathrm{CoL_3}$ in aerobic aqueous solution affords a small yield of the trimeric product. It appears that $[\mathrm{Co}(\mathrm{CoL_3})_2]^{3+}$ is the stable end product of the reactions of several derivatives of the $\mathrm{CoL_3}$ core.[11]

Acknowledgment. Financial support by the National Science Foundation, Grant No. CHE79-26497, is gratefully acknowledged. We thank Paul R. Butler for his important contributions to this research.

Supplementary Material Available: Listings of interatomic distances (Table A), bond angles (Table B), hydrogen atom positional parameters (Table C), thermal parameters (Table D), and observed and calculated structure factors (Table E) (53 pages). Ordering information is given on any current masthead page.

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(21) Elder, R. C.; Florian, L. R.; Lake, R. E.; Yacynych, A. M. *Inorg. Chem.* **1973**, *12*, 2690–2699.

(22) Rabinowitz, H. N.; Karlin, K. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 1420–1426.

Contribution from the Department of Chemistry,
Sogang University, Seoul, 121 Korea

Cationic Iridium(I) and Dihydridoiridium(III) Complexes of Unsaturated Nitriles and Their Catalytic Activities

Soon Heum Park, Hwa-Kun Park, and Chong Shik Chin*

Received August 6, 1984

We have investigated the catalytic hydrogenation and polymerization of the unsaturated nitrile $\mathrm{CH_2{=}CHCN}$ with $\mathrm{M(ClO_4)(CO)(PPh_3)_2}$ (M = Rh, Ir)[1] in which the $\mathrm{ClO_4}$ group is so labile[2] that it is readily replaced by $\mathrm{CH_2{=}CHCN}$ to give the cationic complex $[\mathrm{M(CH_2{=}CHCN)(CO)(PPh_3)_2}]\mathrm{ClO_4}$.[1]

We now report the synthesis of new cationic iridium(I) and dihydridoiridium(III) complexes of unsaturated nitriles, $[\mathrm{IrL(CO)(PPh_3)_2}]\mathrm{ClO_4}$ (**1**) and $[\mathrm{Ir(H)_2L(CO)(PPh_3)_2}]\mathrm{ClO_4}$ (**2**) (L = *cis*-crotononitrile (*cis*-$\mathrm{CH_3CH{=}CHCN}$), *trans*-crotononitrile (*trans*-$\mathrm{CH_3CH{=}CHCN}$), allyl cyanide ($\mathrm{CH_2{=}CHCH_2CN}$)), and their catalytic activities for hydrogenation and isomerization of L. Complexes **1** and **2** have been prepared according to eq 1 and 2.

$$\mathrm{Ir(ClO_4)(CO)(PPh_3)_2 + L \rightarrow \underset{\mathbf{1}}{[IrL(CO)(PPh_3)_2]ClO_4}} \quad (1)$$

$$\mathrm{\mathbf{1} + H_2 \rightarrow \underset{\mathbf{2}}{[Ir(H)_2L(CO)(PPh_3)_2]ClO_4}} \quad (2)$$

$$\mathrm{L} = (\mathbf{a})\ cis\text{-}\mathrm{CH_3CH{=}CHCN},\ (\mathbf{b})\ trans\text{-}\mathrm{CH_3CH{=}CHCN},\ (\mathbf{c})\ \mathrm{CH_2{=}CHCH_2CN}$$

Spectral Data and Structures

Infrared spectral data for **1** and **2** are given in Table I. These clearly suggest that the unsaturated nitriles are coordinated to iridium through the nitrogen, rather than through the π system of the nitrile group. It is well-known that ν_{CN} of a nitrile increases upon coordination through the nitrogen[3,4] and decreases upon

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(1) (a) Woo, J. C.; Kim, S. H.; Chin, C. S. *J. Polym. Sci. Polym. Chem. Ed.* **1982**, *20*, 1948. (b) Kwon, T.; Woo, J. C.; Chin, C. S. *Polyhedron* **1983**, *2*, 1225.

(2) (a) Peone, J.; Vaska, L. *Angew, Chem., Int. Ed. Engl.* **1971**, *10*, 511. (b) Vaska, L.; Peone, J. *Suom. Kemistil. B* **1971**, *44*, 317.

(3) Bryan, S. J.; Huggett, P. G.; Wade, K.; Daniels, J. A.; Jenning, J. R. *Coord. Chem. Rev.* **1982**, *44*, 149 and references therein.

(4) Klinger, M. *Adv. Organomet. Chem.* **1971**, *10*, 115.