ively) which are no longer associated with water or cations. A corresponding small increase is noted for O(3) (1.68 (1)- to 1.70 (1) Å) which is so involved (see Tables III and IV). There is a simultaneous decrease of the Mn(II)-O(3) internuclear distance upon dehydration, corresponding to the movement of the Mn(II) ions to a position closer to the plane of its nearest O(3) neighbors and to conformational changes in the six-oxygen windows.

In general, the (Si,Al)-O-(Si, Al) framework bond angles of hydrated Mn[A] (see Table VI) are very similar to those in Na[A],[16] which can be considered the least strained[1] framework orientiation. Upon dehydration, however, large changes (see Table VI) are observed which can be compared with those found in Tl(I)[1]- and Co(II)[2]- exchanged samples of zeolite A.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. GP-38639X) and by the U. S. Army Research Office, Durham, N. C. We are also indebted to the NSF for its assistance (Grant No. GP-18213) in the purchase of the diffractometer, to Mr. Kevin B. Kunz for performing the Mn(II) ion-exchange experiments, and to the University of Hawaii Computing Center.

Registry No. Mn[A], 42610-91-3.

Supplementary Material Available. Listings of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-723.

Contribution Number 4718 from the Arthur Amos Noyes Laboratory
of Chemical Physics, California Institute of Technology, Pasadena, California 91109

Linkage Isomerism of a Bridging Cyanide. Crystal Structure of Pentacyanocobalt(III)-μ-isocyano-pentaamminecobalt(III) Monohydrate

FRANK R. FRONCZEK and WILLIAM P. SCHAEFER*

Received June 27, 1973

The crystal structure of $(NH_3)_5CoCNCo(CN)_5 \cdot H_2O$ has been investigated by single-crystal X-ray techniques. Of the several crystalline modifications prepared, a form was chosen for study which is isostructural with its linkage isomer $(NH_3)_5CoNCCo(CN)_5 \cdot H_2O$. The space group is *Pbca* with $Z = 8$ and lattice constants are $a = 17.399$ (4), $b = 12.187$ (2), and $c = 13.931$ (1) Å. The calculated density is 1.696 g cm^{-3}, and the measured density is 1.68 (2) g cm^{-3}. Intensity data for 1822 reflections were measured with a Datex automated GE diffractometer using Co Kα radiation. The structure was refined by full-matrix least-squares methods to a final R index of 0.085. This study confirms that, as in the linkage isomer, there is no scrambling of unlike ligands around the two cobalt centers; in this isomer the bridging cyanide group is carbon bonded to the pentaamminecobalt species and nitrogen bonded to the pentacyanocobalt species. In general this compound exhibits longer Co–ligand distances and significantly shorter C–N distances than does its linkage isomer. The molecule is somewhat more symmetrically bent than is its linkage isomer, and a 0.03-Å shortening of the Co–C bond trans to the bridging cyanide group is noted relative to the equatorial Co–C distances. There is also some indication of a lengthening of Co–ligand distances cis to the bridging group at both cobalt atoms of this structure relative to those found in the structure of the linkage isomer.

Introduction

The crystal structure of $(NH_3)_5CoNCCo(CN)_5 \cdot H_2O$ (hereafter referred to as the cyano isomer) has been reported;[1] the molecule has a distinctly nonlinear cyano bridge and exhibits a significant shortening of the Co-N distance trans to the bridging group. Recently de Castello, Mac-Coll, and Haim have reported the synthesis of the isocyano linkage isomer by the reaction in solution[2]

$$[(NH_3)_5CoCN]^{2+} + [(CN)_5CoOH_2]^{2-} \rightarrow (NH_3)_5CoCNCo(CN)_5 + H_2O$$

The structure of this new compound was of particular interest to us due to the unique geometry of the cyano isomer. A comparison of the structure of both isomers would exhibit the effects of linkage isomerism of the cyanide ligand on bonding in both the pentaamminecobalt(III) system and the pentacyanocobalt(III) system. In order to make this comparison, to confirm that ammine and cyanide ligands are not scrambled among the two cobalt centers, and to confirm the orientation of the bridging cyanide group, a structural study of the isocyano isomer was undertaken.

Experimental Section

A sample of the compound was provided by Haim in the form of a finely divided yellow powder. Recrystallization of this powder from an ethanol–water mixture yielded tetragonal crystals of space group $P4_2$ having two molecules per unit cell with dimensions $a = 8.08$ and $c = 14.66$ Å. These crystals lost solvent and disintegrated readily upon removal from the mother liquor. Intensity data were collected for this modification with a diffractometer, but the crystal underwent anisotropic decay in the X-ray beam, and the data obtained were not of suitable quality to allow even the general features of the structure to be determined.[3]

Prismatic crystals were obtained from an aqueous acetic acid solution and were found to be orthorhombic with approximate cell dimensions $a = 11.4$, $b = 10.7$, and $c = 14.5$ Å. Systematic extinctions do not uniquely determine the space group of this form, but density and point symmetry considerations limit the possibilities to $Cmc2_1$ or $C2cm$. These crystals also lost solvent readily and disintegrated upon removal from the mother liquor.

Small, stable crystals of space group *Pbca* were obtained by recrystallization by slow evaporation from a concentrated $NaHCO_3$ solution. Oscillation and Weissenberg photographs indicated that

---

(1) B. C. Wang, W. P. Schaefer, and R. E. Marsh, *Inorg. Chem.*, 10, 1492 (1971).

(2) R. A. de Castello, C. P. Mac-Coll, and A. Haim, *Inorg. Chem.*, 10, 203 (1971).

(3) M. U. Wimbrow and B. L. Trus, unpublished work at California Institute of Technology.

the unit cell dimensions were approximately the same as those of the *Pbca* modification of the cyano isomer. A crystal of dimensions 0.08 × 0.04 × 0.06 mm, elongated along *a*, was chosen for intensity data collection. This crystal was mounted with its *a* axis inclined about 1.5° from the ϕ axis of a Datex automated General Electric quarter circle diffractometer. Cell dimensions were obtained from a least-squares fit of 2θ values measured for 17 reflections, using Co Kα radiation filtered with iron foil (λ 1.7902 Å). The density was experimentally determined by flotation in a CCl_4–$CHBr_3$ mixture.

Intensity data were collected employing Co Kα radiation and a θ–2θ scan technique with a proportional counter. The take-off angle was 3°. Two octants of data were measured, the symmetrically equivalent *hkl* and $\overline{hkl}$ sets. The *hkl* data were measured at a scan speed of 1°/min with backgrounds counted for 40 sec at both extremes of the scan, and the $\overline{hkl}$ data were measured at 0.5°/min with background counting times of 60 sec. Scan widths varied linearly with 2θ, having values of 1.25° at $2\theta = 16°$ and 2.0° at $2\theta = 100°$. The center of the scan was at that 2θ value calculated from the weighted mean of α_1 and α_2 peaks. All reflections with peak centers within 2θ limits of 4 and 153° were measured. Two standard reflections were remeasured every 50 reflections, the same standards being used for both octants, and no significant decrease in the intensities of these check reflections was observed. The two data sets were corrected for background and Lorentz and polarization effects, placed on a common scale, and averaged.

Absorption corrections were not made, as the maximum and minimum possible values of I/I_0 are 0.915 and 0.850. Observational variances were computed from counting statistics with an additional empirical correction term $[(0.02S)^2$, where S is the scan count], to account for nonstatistical errors.[4] We have found the factor 0.02 to be appropriate in this laboratory. Average F's less than zero were set equal to zero with zero weight in subsequent calculations, and systematic absences for this space group were deleted ($0kl = k$ odd, $h0l = l$ odd, $hk0 = h$ odd). Of 2295 measured reflections, 309 were systematic extinctions, only 7 of which had $F > 3\sigma(F)$. Of the 1986 remaining reflections, 1822 had $F > 0$.

Structure Refinement

By comparison of the crystal data included in Table I and comparison of Weissenberg photographs of the cyano and isocyano crystals, it was obvious that the two crystals were isostructural. The only significant difference in cell dimensions is the length of the *a* axis, which is 0.04 Å (8σ) longer in the case of the isocyano structure. Weissenberg photographs of *h0l*, *h1l*, *h2l*, and *h3l* reciprocal lattice nets for the two structures were indistinguishable to the casual observer. A reasonable scale factor for the data was obtained by comparison to the final structure factors of the cyano structure, and the R index calculated using these final cyano structure factors and the measured isocyano data was 13.6%. This structure was refined by full-matrix least-squares methods without exchanging the bridging C and N atoms to their expected identities; hydrogen atoms were assigned $B = 5.0$ and not refined. All machine calculations were carried out on an IBM 370/155 computer using the CRYM crystallographic computing system. Scattering factors for Co, C, N, and O were taken from the International Tables,[5] the values for neutral cobalt being corrected for the real term of anomalous dispersion. Hydrogen scattering factors were those of Stewart, Davidson, and Simpson for bonded hydrogen.[6] The quantity minimized in the least-squares calculations was $\Sigma w(F_o^2 - (1/k^2)F_c^2)^2$, where the weights are $w = 1/\sigma^2(F_o^2)$. After three cycles of least-squares refinement it became apparent that the orientation of the bridging group should be reversed. The anisotropic temperature factors of the two bridging atoms were unreasonable, and a difference map in the Co–C–N–Co plane showed the carbon atom to be in a region of positive electron density and the nitrogen atom to be in a region of negative density of somewhat greater than 1 e Å^{-3}. Therefore, identities of the two atoms were interchanged to the isocyano configuration, and refinement was continued. Hydrogen positions were adjusted on the basis of difference maps in the appropriate planes but were not refined by least squares. A secondary extinction factor was placed into the refinement, and after a few further cycles, convergence was reached with no parameter shifting by more than 30% of its standard deviation. The final matrix contained 182 parameters, corresponding to a data to parameter ratio of 10.0. The final R index ($R = \Sigma \left| F_o - |F_c| \right| / \Sigma F_o$) is 0.085, the final "goodness-of-fit" $(\Sigma w(F_o^2 - F_c^2)/(m - s))^{1/2}$ is 1.76, and the final value of the secondary extinction factor is 0.34 (4) × 10^{-5}. A three-dimensional difference Fourier synthesis calculated at the conclusion of the refinement indicated no discrepancies greater than 0.4 e Å^{-3}. Final structure factors are given in a separate table.[7]

Results and Discussion

On the basis of infrared, visible, and ultraviolet spectra, the isocyano isomer was characterized as a singly bridged binuclear molecule with $(C)_5(N)$ and $(N)_5(C)$ environments about the two cobalt atoms.[2] Our structure refinement confirms this characterization.

Interpretation of results of diffraction studies of transition metal cyanides in terms of bonding is in general not straightforward, due to the possible effects of both ligand-to-metal σ bonding and metal-to-ligand π^* back-bonding. The issue is usually further confused by possible effects of packing upon molecular geometry. The fact that crystals of the isocyano complex were obtained which are isostructural with those of the cyano complex is very fortunate, since this allows us to assume that intermolecular interactions are equal in the two structures and that differences in geometry noted are due only to differences in bonding in the two molecules. The effect of switching the bridging ligand from the cyano to the isocyano orientation appears to be generally a weakening of metal–ligand bonding and a strengthening of C–N bonding both in the terminal and bridging cyanide ligands.

Figure 1 is a stereoscopic view of the isocyano molecule, exhibiting the thermal ellipsoids and the conformations of the ammine ligands. Figure 2 is a comparison of the cyano and isocyano molecules in the same orientation as Figure 1. The thermal motions of the two isomers are seen to be quite similar, with rms amplitudes roughly 30% larger in the isocyano structure. The conformations of the ammines in the two structures are seen to be essentially the same except for that at N(9). This ammine group was not particularly clear in the difference maps calculated at various stages in the refinement; the conformation in the cyano structure fits the intricate hydrogen-bonding system much better. We attribute our failure to determine the positions of these hydrogen atoms unambiguously to the fact that N(9) has the largest thermal motion of the ammine nitrogen atoms, and seems to be moving in and out of the "pocket" formed by cyanide ligands C(3)–N(3) and C(5)–N(5).

Figure 3 exhibits the bond distances and bridging angles of both the cyano and isocyano molecules. Standard deviations are estimated to be 0.005 Å for Co–ligand distances and 0.007 Å for a C–N distance in the cyano structure. Corresponding esd's in the isocyano structure are 0.007 Å for Co–ligand distances and 0.010 Å for C–N distances. Bond angles for the isocyano structure are given in Table III.

The Bridging Cyanide Group

"Inorganic symbiosis" considerations[8] predict that the isocyano linkage is slightly less stable than the cyano, since the harder, more electronegative nitrogen end of the bridging cyanide is bonded to the soft pentacyanocobalt group and the softer carbon end is bonded to the hard pentaamminecobalt group. From the results of the isocyano refinement, metal–ligand bonding does seem to be weaker in this isomer. The results of the cyano structure determination led to the conclusion that the carbon end of the cyano group is a some-

---

(4) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

(5) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

(6) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(7) See paragraph at end of paper regarding supplementary material.

(8) C. K. Jorgensen, *Inorg. Chem.*, 3, 1201 (1964).

Table I. Comparison of Crystal Data

	Cyano	Isocyano
Formula	$(NC)_5CoCNCo(NH_3)_5 \cdot H_2O$	$(NC)_5CoNCCo(NH_3)_5 \cdot H_2O$
Formula weight	376.86	376.86
F_{000}	1501	1501
Space group	*Pbca*	*Pbca*
a axis, Å	17.359 (5)	17.399 (4)
b axis, Å	12.187 (3)	12.187 (2)
c axis, Å	13.936 (3)	13.931 (1)
d_m, g cm^{-3}	1.66 (2)	1.68 (2)
d_x, g cm^{-3}	1.699	1.696
No. of data	1791	1822
R	0.044	0.085
Goodness of fit	1.32	1.76
Crystal size, nm	0.16 × 0.07 × 0.08	0.08 × 0.04 × 0.06

Table II

Positional and Thermal Parameters for Heavy Atoms[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	12970 (7)	66957 (10)	2137 (8)	211 (5)	489 (9)	280 (6)	−16 (12)	21 (10)	53 (14)
Co(2)	11692 (6)	38569 (9)	26567 (8)	184 (4)	444 (9)	274 (6)	2 (12)	0 (9)	−53 (14)
N(1)	10051 (34)	57081 (51)	12591 (39)	257 (27)	544 (56)	287 (37)	−94 (63)	−94 (50)	52 (73)
C(1)	9738 (40)	50553 (66)	18213 (48)	202 (30)	623 (72)	234 (41)	−97 (71)	−41 (56)	91 (91)
C(2)	16196 (43)	76372 (62)	−7724 (54)	217 (31)	418 (65)	376 (47)	29 (74)	58 (60)	−193 (92)
N(2)	18295 (38)	81867 (58)	−13762 (47)	333 (30)	609 (66)	566 (49)	42 (73)	175 (63)	458 (96)
C(3)	11116 (41)	55812 (60)	−7208 (49)	195 (30)	491 (61)	302 (42)	21 (75)	−48 (62)	263 (88)
N(3)	10117 (38)	49570 (57)	−12966 (45)	363 (33)	621 (66)	519 (46)	14 (74)	−142 (63)	−305 (93)
C(4)	14878 (44)	78527 (70)	10999 (53)	203 (31)	646 (74)	371 (49)	27 (81)	54 (61)	101 (102)
N(4)	16129 (39)	85417 (58)	16255 (51)	345 (32)	825 (78)	621 (53)	−25 (77)	−161 (65)	−579 (102)
C(5)	23346 (40)	61882 (65)	3292 (50)	202 (31)	561 (66)	324 (42)	−71 (72)	20 (56)	0 (98)
N(5)	29476 (35)	58933 (54)	3644 (46)	237 (27)	706 (67)	535 (47)	84 (69)	−22 (58)	74 (91)
C(6)	2758 (45)	72269 (62)	527 (49)	286 (32)	547 (68)	242 (46)	99 (75)	11 (59)	−2 (85)
N(6)	−3190 (37)	75481 (59)	−603 (47)	275 (28)	932 (71)	487 (49)	424 (79)	−13 (60)	−33 (93)
N(7)	14546 (35)	25910 (49)	34676 (43)	265 (27)	491 (55)	446 (41)	31 (63)	−150 (54)	60 (78)
N(8)	7394 (33)	46378 (48)	37773 (39)	211 (25)	436 (53)	367 (39)	−178 (59)	44 (48)	821 (73)
N(9)	15977 (33)	31032 (53)	15246 (44)	239 (27)	804 (71)	443 (43)	−153 (68)	−261 (54)	−425 (90)
N(10)	1580 (33)	31791 (45)	23989 (41)	223 (25)	491 (52)	369 (37)	28 (56)	40 (48)	−21 (79)
N(11)	21765 (32)	45182 (48)	29426 (40)	221 (24)	512 (55)	362 (39)	139 (39)	17 (48)	−113 (75)
O(1)	7322 (30)	8057 (42)	18097 (36)	336 (25)	668 (53)	489 (36)	95 (58)	39 (47)	180 (68)

Positional Parameters Assigned to Hydrogen Atoms[b]

	x	y	z		x	y	z
H(1)	1946	2311	3227	H(10)	−103	3650	1927
H(2)	1494	2862	4135	H(11)	−103	3108	3026
H(3)	1062	2032	3377	H(12)	260	2447	2124
H(4)	1147	4891	4136	H(13)	2531	4288	2441
H(5)	410	4103	4110	H(14)	2328	4283	3573
H(6)	439	5256	3512	H(15)	2118	5322	2887
H(7)	1327	2407	1467	H(16)	1171	509	1465
H(8)	2147	2982	1669	H(17)	767	582	2492
H(9)	1522	3565	998				

[a] Temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. All values have been multiplied by 10^5. [b] All values have been multiplied by 10^4.

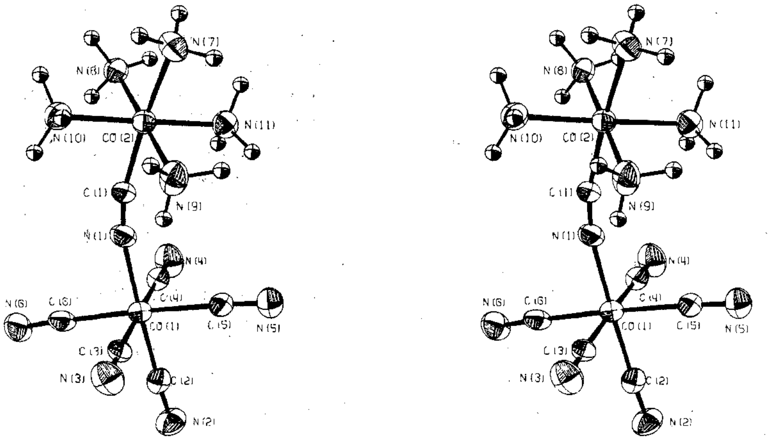


Figure 1. An ORTEP stereopair of the isocyano molecule. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented by spheres of arbitrary radius.

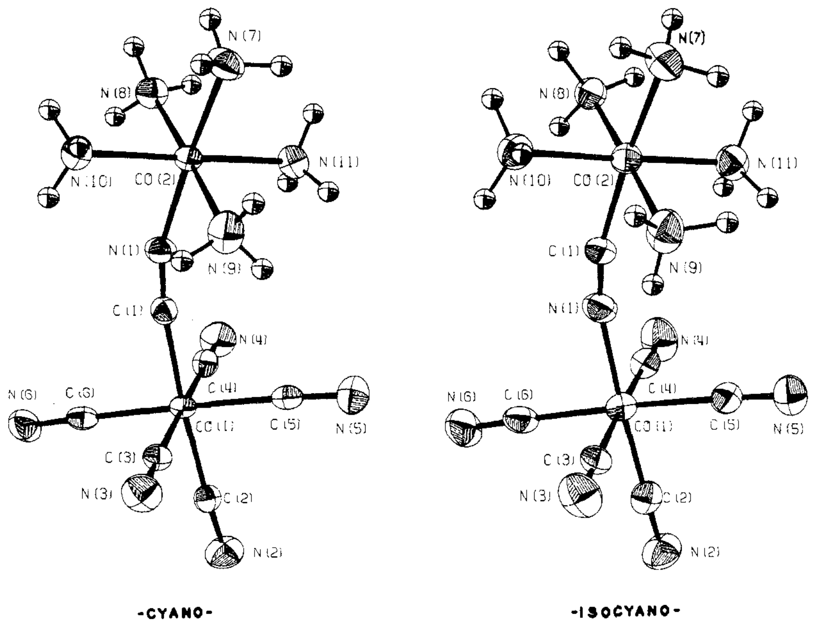


Figure 2. ORTEP drawings of both isomers. Thermal ellipsoids are drawn at the 50% probability level.

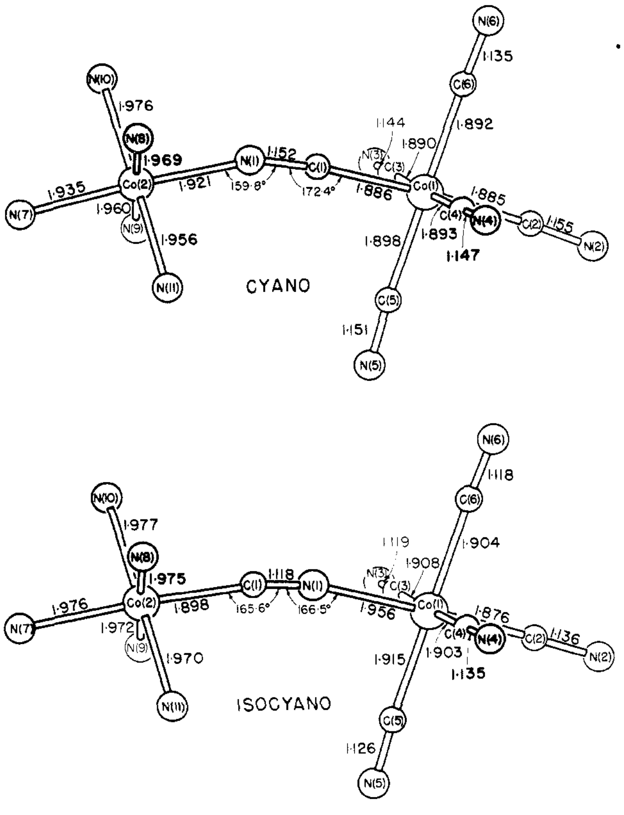


Figure 3. Numbering scheme, bond distance, and bridging angles for both linkage isomers.

what better π accepting ligand than is the nitrogen end, and that observation is confirmed by this study. The Co-bridging C distance is 0.058 Å shorter than the Co-bridging N distance in the isocyano structure, the same trend as was seen in the cyano structure. The Co-N distance itself, however, is significantly longer (0.035 Å) in the isocyano linkage than in the cyano linkage, indicating weaker overall bonding to the pentacyanocobalt group by the nitrogen end of cyanide than to pentaamminecobalt. This weakened metal-to-ligand bonding is accompanied by a strengthening of the bonding within the bridging cyanide itself, as seen in the 0.034-Å shortening of the isocyano C-N distance relative to the cyano distance. This shortening is 4σ and therefore significant. The observed bridging C-N distances correlate well with C-N stretching frequencies in the infrared spectra of these two compounds, supporting the significance of the shortening. The cyano bridge has a C-N distance close to that found in gaseous cyanides and transition metal hexacyanides and is slightly longer than the average distance of 1.13 Å observed in bridging cyanides.[9] The corresponding infrared absorption is at 2180 cm^{-1}, while that for the shorter isocyano bridge is at 2202 cm^{-1}.[10] Lengthening of metal-cyanide distances coupled with shortening of the C-N distance is consistent with the observation that decreased d-π^* back-bonding has the effect of removing electron density from antibonding orbitals of the cyanide group and thus increasing the C-N bond order.

Table III. Bond Angles

Atoms	Angle, deg	Atoms	Angle, deg
N(1)-Co(1)-C(2)	177.6 (3)	C(1)-Co(2)-N(7)	175.2 (3)
N(1)-Co(1)-C(3)	91.5 (3)	C(1)-Co(2)-N(8)	92.6 (3)
N(1)-Co(1)-C(4)	91.0 (3)	C(1)-Co(2)-N(9)	86.3 (3)
N(1)-Co(1)-C(5)	89.1 (3)	C(1)-Co(2)-N(10)	92.9 (3)
N(1)-Co(1)-C(6)	93.1 (3)	C(1)-Co(2)-N(11)	88.2 (3)
C(2)-Co(1)-C(3)	89.2 (3)	N(7)-Co(2)-N(8)	91.1 (3)
C(2)-Co(1)-C(4)	88.3 (3)	N(7)-Co(2)-N(9)	89.9 (3)
C(2)-Co(1)-C(5)	88.7 (3)	N(7)-Co(2)-N(10)	90.1 (3)
C(2)-Co(1)-C(6)	89.1 (3)	N(7)-Co(2)-N(11)	88.9 (3)
C(3)-Co(1)-C(4)	177.4 (3)	N(8)-Co(2)-N(9)	178.9 (3)
C(3)-Co(1)-C(5)	89.2 (3)	N(8)-Co(2)-N(10)	90.5 (2)
C(3)-Co(1)-C(6)	90.2 (3)	N(8)-Co(2)-N(11)	88.9 (3)
C(4)-Co(1)-C(5)	91.2 (3)	N(9)-Co(2)-N(10)	89.8 (3)
C(4)-Co(1)-C(6)	89.3 (3)	N(9)-Co(2)-N(11)	90.9 (3)
C(5)-Co(1)-C(6)	177.8 (3)	N(10)-Co(2)-N(11)	178.7 (3)
Co(1)-N(1)-C(1)	166.5 (6)		
Co(2)-C(1)-N(1)	165.6 (7)		
Co(1)-C(2)-N(2)	178.1 (7)		
Co(1)-C(3)-N(3)	177.2 (6)		
Co(1)-C(4)-N(4)	179.0 (7)		
Co(1)-C(5)-N(5)	177.7 (7)		
Co(1)-C(6)-N(6)	178.5 (6)		

(9) D. Britton, *Perspect. Struct. Chem.*, 1, 109 (1967).

(10) R. A. De Castello, C. P. Mac-Coll, N. B. Egen, and A. Haim, *Inorg. Chem.*, 8, 699 (1969).

The bond angles of the bridging cyano group are worthy of note. Perhaps the most surprising result of the cyano structure determination was that the molecule is distinctly nonlinear, the sum of the Co-N-C and N-C-Co bond angles deviating about 28° from linearity. This effect is thought to be due to the two oppositely charged ends of the neutral molecule attempting to achieve optimum intramolecular interactions rather than to any change in the bonding character of the bridging group, as such bonding changes would lead to an increased C-N distance. In the isocyano structure, the extremely short C-N distance indicates even more strongly that no contribution from a structure such as $:C{=}\dot{N}:-$ caused this bending; however, these results shed little light on the intramolecular hypothesis. It is interesting to note that the isocyano bridge is much more symmetrically bent than the cyano bridge, but the sum of the two angles is the same in both structures to within 0.1°. Differences in bond lengths and angles cause the Co-Co distance in the isocyano isomer, 4.767 Å, to be considerably shorter than the corresponding distance of 4.843 Å in the cyano molecule.

The Pentaamminecobalt Group

The overall geometry of this group agrees fairly well with that of the $[(NH_3)_5CoCN]^{2+}$ ion, which has been determined by X-ray studies of the chloride[11,12] and perchlorate[12] salts. All Co-N distances of the $Co(NH_3)_5$ group in the isocyano molecule are identical within experimental error, having an average value of 1.974 (2) Å, which is slightly longer (on the borderline of statistical significance) than the average value of 1.962 Å found in the most precise determinations of cobalt pentaammine structures.[13] All equatorial Co-N distances are equal to or longer than the corresponding distances in the cyano molecule. No particular distance is longer by a statistically significant amount; however, the trend is striking and hints at significance.

In the cyano molecule, a 0.03-Å shortening of the Co-N distance trans to the bridging group was noted. Comparison of the axial Co-N distances of the two isomers indicates that with the reversed orientation of the bridging group this effect has disappeared. This result is rather surprising in light of our former beliefs about the cause of this shortening, which invoked some π-accepting character on the part of the nitrogen end of the cyano bridge.[1] If this were the case, an even more pronounced shortening should be noted for the isocyano isomer, due to the greater π-bonding ability of carbon-bonded cyanide. However, as is the case for most cobalt pentaammines, no shortening is observed in the isocyano structure. A possible explanation for this phenomenon is competition between the cyano group and the trans ammine for the σ bonding e_g orbitals of the cobalt atom. A similar situation is seen in the $[Co_2(CN)_{10}]^{6-}$ anion, in which a Co-Co σ bond is thought to compete successfully with a trans cyanide causing an elongation of the Co-C distance.[14,15] In the present system, the ammine appears to win the competition over N-bonded cyanide and compete about equally with C-bonded cyanide. This explanation forces the conclusion that if σ competition is the most important contributing factor, not only is C-bonded cyanide a better π acceptor than N-bonded cyanide but also a better σ donor.

The Pentacyanocobalt Group

The average equatorial Co-C and C-N distances in the isocyano molecule are 1.908 (4) and 1.125 (7) Å, respectively. In the cyano molecule, the corresponding distances are 1.893 (2) and 1.144 (5) Å. While the individual differences are not significant statistically in all cases, the term by term trend appears clear; the effect of switching the bridging ligand to the isocyano form lengthens the equatorial Co-C distances and shortens the equatorial C-N distances. The sums of the two are the same within experimental error in all cases. While both Co-C σ- and π-bonding lead to shortening of the Co-C distance, Co-C σ bonding results in a decrease in the C-N distance, while Co-C π bonding leads to a compensatory increase in the C-N distance, resulting in very uniform terminal C-N distances in a wide variety of cyanides. In this system the observed differences indicate similar metal-ligand σ bonding in both isomers and greater π bonding in the equatorial ligands of the cyano isomer. Since the effect is rather small, this is not inconsistent with results of MO calculations and vibrational studies which indicate that π bonding in $[Co(CN)_6]^{3-}$ is relatively unimportant with respect to σ bonding.[16,17] This observed shortening of equatorial C-N distances caused by N bonding to the bridging group is also consistent with the infrared spectra of the two isomers. The terminal cyanide stretching frequency for the cyano isomer occurs at 2120 cm^{-1}, while the corresponding absorption in the isocyano spectrum occurs at 2131 cm^{-1}, indicating stronger C-N bonding in the isocyano molecule.[2,10,18]

In the cyano molecule, all Co-C distances of the pentacyanocobalt group are equivalent; however, in the isocyano molecule, a shortening of the axial Co-C distance by 0.032 Å relative to the equatorial distances is noted. This shortening is 4σ and therefore quite significant. This observation seems to support the contention that nitrogen-bonded cyanide is a poorer σ donor than carbon-bonded cyanide, since the C-bonded terminal ligand competes successfully for cobalt e_g orbitals with the N-bonded bridging group. The significance of this apparent shortening is diminished, however, when the two isomers are compared. This distance is insignificantly different from the corresponding distance in the cyano isomer, which has normal equatorial Co-C distances. The overall effect upon the pentacyanocobalt system caused by switching the bridging group to the isocyano form is best thought of as a lengthening of the cis ligand distances only, with no effect on the trans distance.

Acknowledgments. We are very grateful to Professor Haim for supplying the compound, to Dr. Gary Christoph for assistance in growing crystals, and to Dr. R. E. Marsh, whose guidance was invaluable.

Registry No. $(NH_3)_5CoCNCo(CN)_5 \cdot H_2O$, 50790-47-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24×

---

[11] J. A. Stanko, private communication.

[12] W. Ozbirn and R. A. Jacobson, *Inorg. Chim. Acta*, 4, 377 (1970).

[13] Reference 1 and additional references cited therein.

[14] G. L. Simon, A. W. Adamson, and L. F. Dahl, *J. Amer. Chem. Soc.*, 94, 7654 (1972).

[15] L. D. Brown, K. N. Raymond, and S. Z. Goldberg, *J. Amer. Chem. Soc.*, 94, 7664 (1972).

[16] L. H. Jones, *Inorg. Chem.*, 2, 777 (1963).

[17] J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, 89, 3356 (1967).

[18] Terminal stretching absorption in the isocyano spectrum actually consists of two bands, at 2128 and 2131 cm^{-1}; however, the 2128-cm^{-1} band can be associated with the nonequivalent trans cyanide.

reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W. Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-727.

Contribution from the Department of Chemistry,
Brown University, Providence, Rhode Island 02912

Crystal and Molecular Structure of Trichloronitrosylbis(methyldiphenylphosphine)ruthenium(II), $RuCl_3(NO)(PMePh_2)_2$

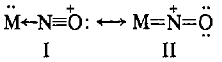
ARTHUR J. SCHULTZ, RICHARD L. HENRY, JOSEPH REED, and RICHARD EISENBERG*[1]

Received June 25, 1973

The crystal and molecular structure of trichloronitrosylbis(methyldiphenylphosphine)ruthenium(II), $RuCl_3(NO)(PMePh_2)_2$, has been determined from three-dimensional X-ray data collected by counter methods using the θ-2θ scan technique. The complex crystallizes in space group $P2_1/c$ of the monoclinic system in a cell of dimensions $a = 12.308$ (4), $b = 16.579$ (6), $c = 14.700$ (4) Å, $\beta = 114.82$ (2)°, and $V = 2728$ Å^3. An experimental density of 1.56 (2) g/cm^3 agrees with a calculated value of 1.55 g/cm^3 for $Z = 4$. The structure was solved by standard heavy-atom methods and has been refined by least squares to a conventional R factor of 0.044. The coordination geometry about the Ru atom is essentially octahedral with the phosphine ligands in trans positions. The nitrosyl is linearly coordinated with an Ru-N distance of 1.744 (6) Å and an Ru-N-O bond angle of 176.4 (6)°. These parameters agree with those reported for other ruthenium(II) nitrosyl complexes and confirm the notion that complexes of the type $RuCl_3(NO)L_2$ where L = tertiary phosphine are best described as NO^+ complexes of Ru(II). The Ru-Cl distance trans to the nitrosyl is shorter than the other Ru-Cl distances in the structure (2.357 (2) Å *vs.* 2.398 (7) Å) and the N-Ru-P bond angles average 94.1 (6)°, thus giving further structural evidence of the strong metal-nitrosyl π interaction in this system. The bonding in $RuCl_3(NO)(PMePh_2)_2$ is compared with that of the isoelectronic complex $RuCl_3(p\text{-}N_2C_6H_4Me)(PPh_3)_2$ whose structure has recently been determined.

Introduction

Ruthenium forms more nitrosyl complexes than any other element, and of these complexes the ruthenium nitrosyl phosphines form a most interesting subset.[2] The first members of this class of complexes were reported in 1966 by Fairy and Irving[3] and by Chatt and Shaw[4] and have the general formula $RuCl_3(NO)L_2$ where L is a tertiary phosphine, arsine, or stibine. These complexes exhibit nitrosyl stretching frequencies in the range 1829-1899 cm^{-1} and are viewed formally as NO^+ complexes of Ru(II). A linear mode of nitrosyl coordination is thus assumed for these systems and resonance structures I and II are used to explain the metal-nitrosyl bonding.



$$\overset{\cdot\cdot}{M}\leftarrow N\equiv\overset{+}{O}: \longleftrightarrow M=\overset{+}{N}=\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}$$

I II

During the last few years interest in nitrosyl complexes has been stimulated by the knowledge that NO can coordinate to transition-metal ions in either a linear or a bent manner[5-24] and that certain nitrosyl complexes have been found to be catalytically active.[25-28] In our laboratory we have been investigating the structures of ruthenium nitrosyl phosphines, and in particular low valent systems which contain metal-nitrosyl units formally assigned as Ru^0-NO^+ [19,23] and Ru^{II}-NO^-.[18] In order to compare the structural parameters obtained in these studies with those of one of the parent Ru^{II}-

---

[1] Address correspondence to this author at Department of Chemistry, University of Rochester, Rochester, N. Y. 14627; Alfred P. Sloan Foundation Fellow, 1972-1974.

[2] For reviews of nitrosyl complexes, see F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1972, p 713-719; B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, 7, 277 (1966); W. P. Griffith, *Advan. Organometal. Chem.*, 7, 211 (1968); B. A. Frenz and J. A. Ibers, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Phys. Chem., Ser. One*, 11, 33 (1972).

[3] M. B. Fairy and R. J. Irving, *J. Chem. Soc. A*, 475 (1966).

[4] J. Chatt and B. L. Shaw, *J. Chem. Soc. A*, 1811 (1966).

[5] P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, 2, 1043 (1963).

[6] S. H. Simonsen and M. H. Mueller, *J. Inorg. Nucl. Chem.*, 27, 309 (1965).

[7] A. Domimcano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Commun.*, 476 (1966).

[8] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 7, 2345 (1968); D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, 90, 4486 (1968).

[9] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 8, 1282 (1969).

[10] B. A. Frenz, J. H. Enemark, and J. A. Ibers, *Inorg. Chem.*, 8, 1288 (1969).

[11] G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1275 (1970).

[12] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 9, 1105 (1970).

[13] D. A. Snyder and D. L. Weaver, *Inorg. Chem.*, 9, 2760 (1970).

[14] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 10, 1035 (1971).

[15] D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *Inorg. Chem.*, 10, 1043 (1971).

[16] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 10, 1479 (1971).

[17] C. G. Pierpont, A. Pucci, and R. Eisenberg, *J. Amer. Chem. Soc.*, 93, 3050 (1971).

[18] C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 11, 1088 (1972); *J. Amer. Chem. Soc.*, 92, 4760 (1970).

[19] C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 11, 1094 (1972).

[20] J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, 11, 1420 (1972).

[21] M. O. Visscher and K. G. Caulton, *J. Amer. Chem. Soc.*, 94, 5923 (1972).

[22] R. Eisenberg, A. P. Gaughan, Jr., C. G. Pierpont, J. Reed, and A. J. Schultz, *J. Amer. Chem. Soc.*, 94, 6240 (1972).

[23] C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 12, 199 (1973).

[24] C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester, and C. A. Reed, *Inorg. Chem.*, 12, 1304 (1973).

[25] J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, 91, 5659 (1969).

[26] J. P. Candlin and W. H. Hanes, *J. Chem. Soc. C*, 1856 (1968).

[27] E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman, *J. Amer. Chem. Soc.*, 92, 528 (1970).

[28] S. T. Wilson and J. A. Osborn, *J. Amer. Chem. Soc.*, 93, 3068 (1971).