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STUDIES ON METAL—METAL BONDS

II *. THE CRYSTAL AND MOLECULAR STRUCTURES AND OTHER PHYSICAL PROPERTIES OF $(\eta^5\text{-}C_5H_5)_2Co_2(NO)_{2-x}(CO)_x$ ($x = 1, 0$). A COMMENT ON THE EAN RULE

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Summary

The compounds $(\eta^5\text{-}C_5H_5)_2Co_2(NO)_{2-x}(CO)_x$ ($x = 1, 0$) crystallize in space group $P2_1/c$ with $Z = 2$ molecules per unit cell. The unit cell constants for the former ($x = 1$) are: a 7.878(5), b 6.121(1), c 12.080(4) Å and β 105.46(2)°; while those for the latter ($x = 0$) are: a 7.883(1), b 6.117(1), c 12.119(3) Å and $\beta = 105.44(2)°$. In both cases the fragment $Co\text{-}\mu_2\text{-}(NO)_{2-x}(CO)_xCo$ is planar, with a maximum deviation of any atom in that fragment from its least squares plane of 0.004 Å. The Cp rings are planar and have normal C—C distances. The perpendiculars to the Cp planes make angles of 90° with the normals to the $Co(NO)_{2-x}(CO)_xCo$ planes. In what followes the values given in parentheses refer to the $x = 0$ derivative, the other values refer to the carbonylnitrosyl derivative ($x = 1$). The range of Co—C(Cp) distances is 2.071 to 2.103 Å, mean 2.088 Å (2.086 to 2.115 Å, mean 2.101 Å). The Cp ring C—C distances range from 1.379 to 1.401 Å, mean 1.388 Å (1.381 to 1.445 Å, mean 1.411 Å). The Co—N (or C) distances are 1.829 and 1.831 Å (1.824 and 1.827 Å). The N—Co—N (or C) angle is 99.3° (99.0°). The two independent values of the Co—N (or C)—O angles are 139.5 and 139.8° (139.4 and 139.6°) while the value of the Co—N(or C)—Co angle is 80.7° (81.1°). The Co—Co distance is 2.370 (2.372) Å. The EAN rule is discussed with regard to these and related observations. The paramagnetic carbonylnitrosyl derivative gives a 15 line ESR spectrum (room temperature, benzene) of which the lines have, approximately,

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* For part I see ref. 6.

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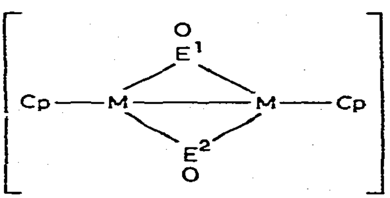
intensity ratios of 1/2/3/···7/8/7···3/2/1, as expected for an unpaired electron distributed equally over two ^{59}Co nuclei. The ^{59}Co hyperfine splitting is 47.4 Oe, the g value is 2.0539 and the linewidth is ca. 29 Oe. At room temperature there is no evidence of a ^{14}N hyperfine splitting from the bridging nitrosyl.

Introduction

In 1968, Brunner [2] prepared the novel compound $Cp_2Fe_2(NO)_2$ for which the existence of a double Fe—Fe bond had to be postulated if the substance were to obey the EAN rule, a fact later verified in the structural study of Calderon et al. [3], who found an Fe—Fe distance of 2.326(4) Å (compared with 2.50—2.70 Å normally found for Fe—Fe single bonds). Later, Brunner [4] prepared the Co analogue by direct nitrosylation of $CpCo(CO)_2$ using NO gas, $Cp_2Co_2(NO)_2$ being the only NO-containing product which could be isolated. Very recently, Müller and Schmitt [5] announced the synthesis of $Cp_2Co_2(CO)(NO)$ obtained by reaction (reflux) of $Cp_2Co_2(NO)_2$ and cobalt carbonyls, and for which no structural data were presented. In an independent study, using *N*-nitrosourea derivatives (i.e., *N*-methyl- or *N*-ethyl-*N*-nitrosourea), Herrmann and Bernal [6] showed smooth, partial nitrosylation of $CpCo(CO)_2$ (boiling benzene) to $Cp_2Co_2(CO)(NO)$. Finally, two recent notes from Bergman [7,8] gave the electrochemical preparation [7] and the structural details of $Cp_2Co_2(CO)_2^-$ which is isoelectronic with $Cp_2Co_2(CO)(NO)$. In this report, we give the structural parameters of $Cp_2Co_2(CO)(NO)$ (III) and $Cp_2Co_2(NO)_2$ (II), the ESR of III and IR spectra of II and III, as well as the usual analytical data. An electrochemical study (cyclic voltammetry) of the carbonylnitrosyl and the dinitrosyl compounds is also presented.

In what follows, it will be desirable to label the various compounds discussed by simple roman numerals:



$Cp = (\eta^5\text{-}C_5H_5)$

(I) $M = Fe$; $E^1 = E^2 = N$; $n = 0$

(II) $M = Co$; $E^1 = E^2 = N$; $n = 0$

(III) $M = Co$; $E^1 = N$; $E^2 = C$; $n = 0$

(IV) $M = Co$; $E^1 = E^2 = C$; $n = -1$

Experimental

Crystallography

The procedures of data collection and processing were so nearly identical that we will describe only that for III; below we give only those details of data collection for II which differ from those of III. Crystals of both substances were obtained by cooling (−35°C) solutions (diethyl ether/methylene chloride, 2/1) of the compounds. In both cases, the crystals chosen had six-sided plate morphology, which upon indexing turned out to be: (100 and $\bar{1}00$; the large face of the flat plates); the six edges of the plates (010 and $0\bar{1}0$); (001 and $00\bar{1}$) and (011 and $0\bar{1}\bar{1}$). A crystal of III was mounted with its [010] direction parallel on the

ϕ axis of the diffractometer. Its dimensions were 0.336 mm along the [001] direction; 0.296 mm along the [010] direction; 0.296 mm along the [011] direction and 0.104 mm along the [100] direction. The crystal was mounted on a computer-controlled CAD-4 diffractometer using Mo-K_α radiation together with a dense graphite monochromator. A total of 23 high-angle reflections ($24° \leqslant 2\theta \leqslant 30°$) were centered automatically and used to define the cell constants. Intensity data were collected using a scan range of $2.40° + 0.80°$ tg θ (θ = calculated peak center) and scan speed between 0.4 to 5.0 deg min^{-1}. The scan speed was decided by a pre-scan of 5 deg min^{-1} in which, if the reflection had more than 60 net counts above background, the reflection was deemed observed and re-scanned at a rate such that a minimum of 2000 counts above background were achieved. The maximum time allowed was five minutes. All of the data between $5° \leqslant 2\theta \leqslant 50.0°$ were scanned. Some of the data between 50.0 and 56.0° were also sampled. In total 1444 reflections were collected of which 1158 were used in the refinement of the structural parameters. The data were corrected for Lorentz and polarization effects which include the effect of the graphite crystal used for monochromatization. They were also corrected for absorption, and the transmission coefficients ranged from 0.44 to 0.73. Solution of the structure was derived from program MULTAN. Refinement of the structural parameters of III gave:

$$R_1(F) = \sum|(|F_o| - |F_c|)|\sum|F_o| = 0.0031$$

$$R_2(F) = [\sum w(F_o - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.0034$$

$$\text{Error of fit} = [\sum w(F_o - |F_c|)^2/(NO - NV)]^{1/2} = 1.12$$

where the weights, w, were set at $1/\sigma^2(F)$ and $\sigma(F_o) = \sigma(I)/2LpF$, where $\sigma(F_o)$, $\sigma(I)$, Lp and F_o are the standard deviations of F and I, the Lorentz-polarization factor and F observed respectively. The $\sigma(I)$ were calculated from simple Poisson statistics. NO and NV are, respectively, the number of observations and the number of variables in the refinement.

The only differences between the above and the details of data collection of II are the following: the crystal was mounted parallel to the [012] direction; and while its morphology was the same as that of III, the crystal dimensions were 0.414 mm along the [001] direction; 0.344 mm along the [011] direction and 0.112 mm along the [100] direction. The transmission coefficients ranged from 0.38 to 0.71 for this crystal. A total of 1557 reflections were collected in the range of $5° \leqslant 2\theta \leqslant 56°$ using Mo-K_α radiation, as described above (i.e., scan lengths, etc. were identical for both cases). The structure was solved by Patterson methods and refinement converged to final discrepancy indices of $R_1(F) = 0.049$ and $R_2(F) = 0.054$, error of fit = 0.86. In both cases the scattering curves used for Co were corrected for anomalous dispersion.

Data decollation was accomplished with a locally written program (Houston) and all other data processing and calculations were carried out with the X-ray '72 system of programs [9]. The X-ray crystallographic data are given in Table 1.

Refinement of the positional and isotropic thermal parameters for the hydrogen atoms was carried out in the case of III, which was not sensible in the case of II. Note in Table 2 (positional and thermal parameters) that, throughout, the

TABLE 1

X-RAY CRYSTALLOGRAPHIC DATA

	III	II
Molecular formula	$C_{10}H_{10}Co_2(CO)(NO)$	$C_{10}H_{10}Co_2(NO)_2$
Molecular weight	306.07	308.07
Space group	$P2_1/c$	$P2_1/c$
Unit cell data		
a	787.8(5) ppm	788.3(1) pm
b	612.1(1) pm	611.7(1) pm
c	1208.0(4) pm	1211.9(3) pm
α	90.00°	89.99(2)° [a]
β	105.46(2)°	105.44(2)°
γ	90.00°	90.02(1) [a]
V	561 A^3	563 A^3
Density (measured), D_m	1.81(2)	1.82(2)
Density (calculated; $Z = 2$), D_c	1.810 g cm^{-3}	1.816 g cm^{-3}
Radiation used for data collection	Mo-K_α	Mo-K_α
Linear absorption coefficient	30.66 cm^{-1}	30.60 cm^{-1}
Crystal shape (dimensions, see text)	Six-sided plate	Six-sided plate
Number of reflections measured	1444	1557
Number used in the final refinement	1158	1178
Number of variables for refinement	93	93

[a] The unit cell dimensions were refined on the assumption the substance was triclinic in order to test the accuracy of the crystal centering.

thermal parameters of the crystal used for the study of II are much higher. Where as in III the hydrogens were found sharply defined in the difference Fourier map at sensible positions, this was not equally the case for II; therefore, we placed them at theoretical positions with fixed thermal parameters. It is remarkable the degree of precision and accuracy with which they were found in the refinement of the data for III, see Table 2 for a comparison of found positions vs. calculated positions.

The bond lengths and angles are listed in Table 3, least squares planes (with deviations thereof) in Table 4. A set of tables of structure factors is available for both compounds *.

In Figs. 1 and 2 the shape of molecules of II and III and the packing in the unit cell are shown.

ESR studies

These were carried out in benzene solutions (approximately 0.05 *M*) using a standard Varian 4502 spectrometer. Magnetic field measurements were made with an NMR magnetometer and the room temperature spectrum is shown in Fig. 3, together with the details of that run [11].

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* A Table of Structure Factors has been deposited as NAPS document number No. 03080 with ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. A copy may be secured by citing the document and remitting $ 3.00 for microfiche and 7.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications. Outside the United States or Canada, postage is $ 2.00 for a photocopy or $ 1.00 for a fiche.

TABLE 2

POSITIONAL AND THERMAL PARAMETERS OF THE ELEMENTS IN $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_{2-x}(CO)_x$ (x = 0, 1)

Each entry is double, the top one corresponds to x = 1 [a]. Standard deviations in parentheses.

Atom	x	y	z	$10^4\,U_{11}$	$10^4\,U_{22}$	$10^4\,U_{33}$	$10^4\,U_{12}$	$10^4\,U_{13}$	$10^4\,U_{23}$
Co	0,11258(7)	0,90736(9)	0,06868(4)	331(3)	411(3)	363(3)	56(4)	80(2)	−27(3)
	0,11814(12)	0,90801(15)	0,06846(7)	444(6)	469(12)	396(8)	48(5)	35(7)	−42(3)
O	0,2371(4)	0,2000(6) [b]	−0,0756(3)	467(20)	957(27)	933(26)	−119(20)	371(20)	305(22)
	0,2331(8)	0,1987(12)	−0,0769(6)	602(44)	1108(53)	1079(47)	−96(37)	365(34)	397(42)
N	0,1272(5)	0,1070(6) [b]	−0,0410(3)	414(21)	603(24)	566(22)	85(23)	107(19)	0(22)
	0,1254(9)	0,1068(11)	−0,0417(5)	572(36)	653(40)	665(37)	0(34)	23(31)	5(33)
C(1) [c]	0,2915(8)	0,9219(11)	0,2325(4)	649(36)	757(38)	510(29)	172(38)	−112(27)	−163(32)
	0,2903(14)	0,9264(18)	0,2331(7)	867(66)	935(70)	587(42)	197(62)	−62(47)	−66(51)
C(2)	0,1800(9)	0,7473(13)	0,2253(5)	617(38)	1034(53)	565(34)	198(40)	138(32)	315(38)
	0,1786(15)	0,7502(22)	0,2278(9)	883(71)	1202(94)	640(56)	62(71)	118(53)	287(63)
C(3)	0,2028(10)	0,6043(11)	0,1412(6)	768(45)	496(35)	863(45)	87(39)	−156(37)	91(38)
	0,2033(16)	0,6023(17)	0,1426(9)	954(74)	634(57)	918(70)	44(60)	−176(60)	230(55)
C(4)	0,3270(9)	0,6964(13)	0,0931(5)	713(34)	1165(60)	570(36)	631(46)	40(34)	−102(38)
	0,3247(16)	0,6904(22)	0,0909(8)	908(80)	1138(89)	635(54)	561(75)	44(54)	−74(58)
C(5)	0,3821(7)	0,8942(12)	0,1497(5)	333(27)	914(43)	744(36)	36(34)	−27(27)	152(40)
	0,3822(12)	0,8948(21)	0,1485(9)	504(48)	1155(88)	751(59)	75(58)	0(35)	263(69)
H(1) [c]	0,302(6)	0.047(8) [b]	0,280(4)	8(2)	8(2)				
	0,3332	0,0467	0,2842						
H(2)	0,117(7)	0,729(10)	0,266(5)	11(3)					
	0,0927	0,7295	0,2767						
H(3)	0,147(7)	0,488(10)	0,122(5)	11(3)					
	0,1459	0,4653	0,1243						
H(4)	0,357(6)	0,639(7)	0,043(4)	7(2)					
	0,3627	0,6286	0,0296						
H(5)	0,461(6)	0,010(8) [b]	0,130(4)	9(2)					
	0,4670	0,9914	0,1324						

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[a] Note that in this compound CO and NO are disordered in the crystal lattice. In the list of coordinates "N" is the average position of C and N; see text for details of refinement. [b] These coordinates should have 1.0 added to them in order for the atoms in question to be located in the same molecule as the other ones. [c] Positions of hydrogens for III are theoretical due to higher thermal motion, see text.

TABLE 3

DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

A. Distances between heavy atoms

Bond	II	III	Bond	II	III
Co—Co	2.372(1)	2.370(1)	Co—C(5)	2.086(9)	2.089(5)
Co—N [a]	1.827(7)	1.829(4)	N—O [a]	1.187(10)	1.200(5)
Co—N	1.824(7)	1.831(4)	C(1)—C(2)	1.381(17)	1.379(10)
Co—C(1)	2.113(8)	2.103(5)	C(1)—C(5)	1.415(16)	1.386(9)
Co—C(2)	2.095(11)	2.071(7)	C(2)—C(3)	1.424(17)	1.389(10)
Co—C(3)	2.115(10)	2.093(7)	C(2)—C(4)	1.385(19)	1.384(11)
Co—C(4)	2.094(13)	2.084(8)	C(4)—C(5)	1.445(18)	1.401(10)

B. C—H distances in Cp rings of III

C(1)—H(1)	0.95(5)
C(2)—H(2)	0.80(7)
C(3)—H(3)	0.84(6)
C(4)—H(4)	0.79(5)
C(5)—H(5)	1.02(5)

C. Angles

Angle	II	III	Angle	II	III
N—Co—N [a]	99.0(3)	99.3(2)	C(1)—C(2)—C(3)	108.8(10)	109.6(6)
Co—N—Co [a]	81.1(3)	80.7(2)	C(2)—C(3)—C(4)	108.8(10)	107.1(6)
Co—N—O [a]	139.4(5)	139.5(3)	C(3)—C(4)—C(5)	106.6(10)	108.0(7)
Co—N—O [a]	139.6(5)	139.8(3)	C(4)—C(5)—C(1)	108.1(10)	107.8(6)
C(5)—C(1)—C(2)	107.6(10)	107.6(6)			

[a] Disordered N, C in III.

TABLE 4

LEAST SQUARES PLANES THROUGH SELECTED ATOMS [a]. DEVIATIONS (Å) OF ATOMS FROM THESE PLANES. ANGLES (°) BETWEEN THE NORMALS OF PAIRS OF THESE PLANES (Equations give carbonyl nitrosyl, then dinitrosyl)

1. Plane defined by Co, (C, N), O, Co*, (C, N)*, O*

$-0.15536x + 0.74016y + 0.65424z = 4.53052$

$-0.15247x + 0.72347y + 0.65116z = 4.54868$

Co	0.00001	0.00001	Co*	−0.00001	−0.00001
O	0.00204	0.00153	O*	−0.00204	−0.00153
(C, N)	−0.00381	−0.00285	(C, N)*	0.00381	0.00285

2. Plane defined by C(1), C(2)---C(5) (Cp ring)

$0.56247x - 0.48338y + 0.67079z = -0.03067$

$0.56816x - 0.47453y + 0.67232z = +0.00675$

C(1)	0.00914	0.00753	C(4)	−0.00257	−0.00940
C(2)	−0.01079	−0.01343	C(5)	−0.00396	0.00114
C(3)	0.00818	0.01416	Co	−1.72317	−1.72408

3. Angle between planes 1 and 2 is 89.64° for CO, NO; and 89.91° for $(NO)_2$.

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[a] Equations are expressed as $px + qy + rz = s$ in orthogonal Å space.

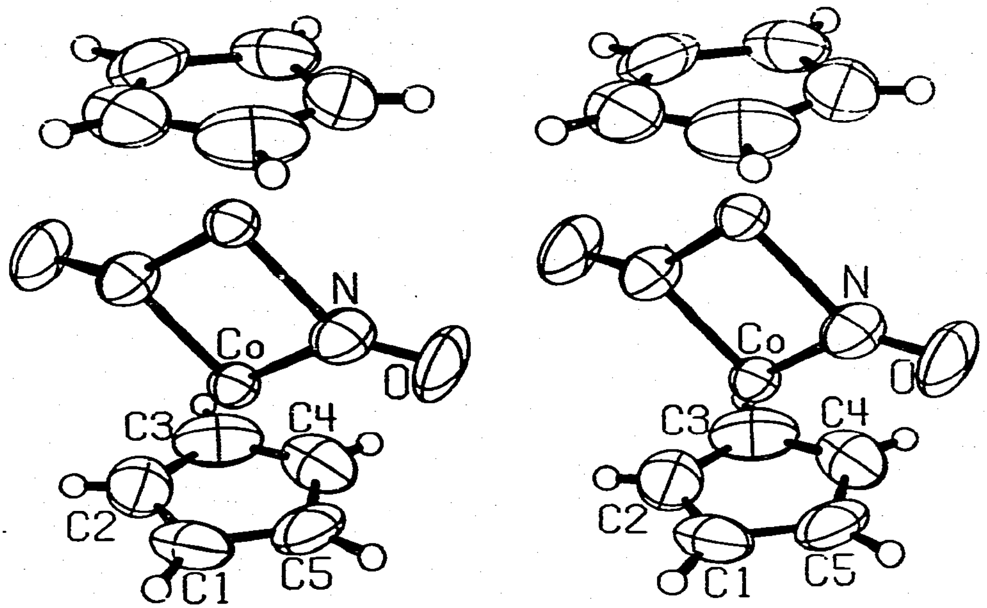

Fig. 1. The shape of both molecules showing the numbering system used in the crystallographic study. This is a stereo pair drawn with 50% probability envelopes for the thermal ellipsoids of the heavy atoms.

Preparation of II and III

Both compounds were prepared and purified according to Brunner (II) [4] and Herrmann (III) [6], respectively.

Description of the molecules and discussion

The distances and angles, as well as the planes, listed in Tables 3 and 4 show that the two molecules are essentially identical. They consist of a pair of cobalt

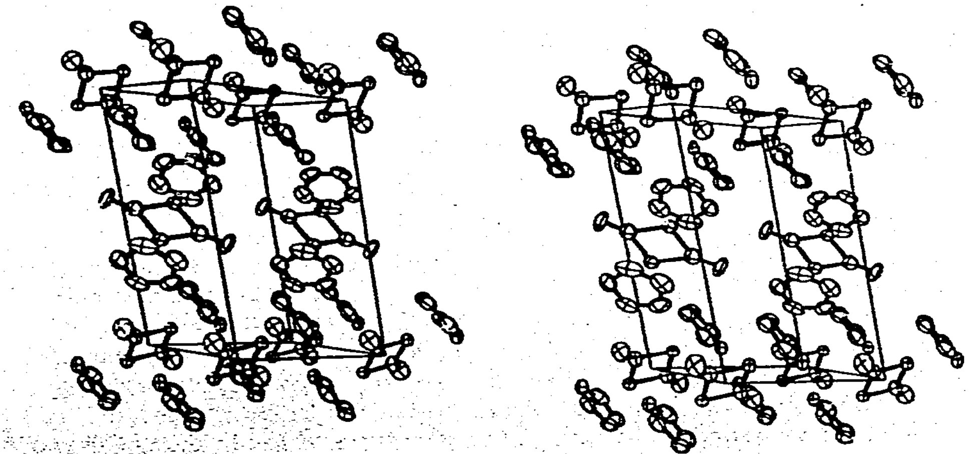

Fig. 2. The packing of the molecules in the unit cell. Hydrogen atoms were omitted for clarity.

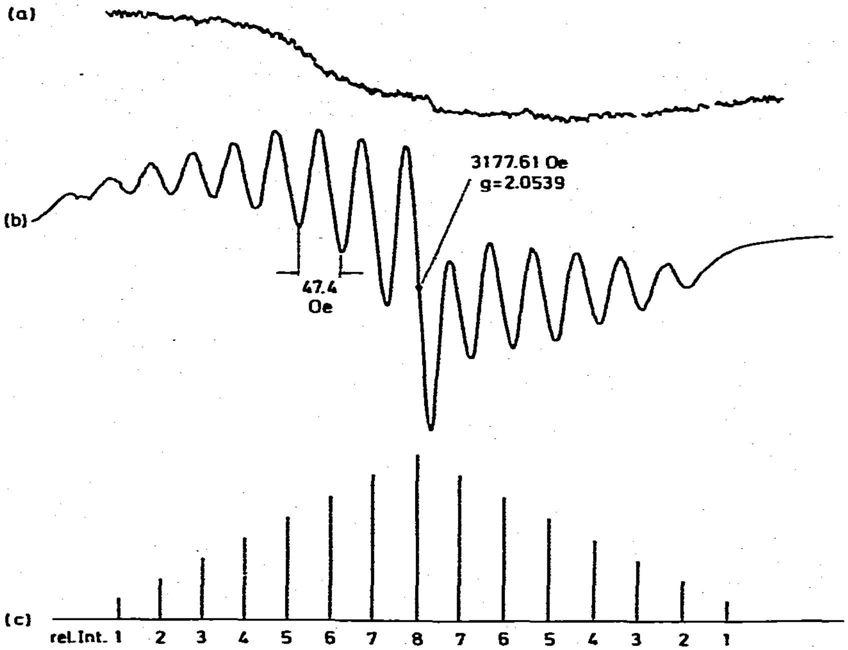

Fig. 3. The ESR spectrum of a benzene solution (about 0.05 *M*) of $Cp_2Co_2(CO)(NO)$ at 20°C. The klystron frequency was 9.13469679 GHz, the width of the total scan ca. 1000 Oe and the center of the scan ca. 3177.61 Oe.

atoms held together by two bridging groups (CO or NO) so as to form a planar $Co_2(NO)_{2-x}(CO)_x$ moiety. The four-membered ring is really diamond shaped, having angles at the Co atom (X—Co—Y; and Y = C or N) of approximately 99° while the Co—(X,Y)—Co angles are only 81° in both cases. The Co—(X,Y) distances and Co—Co distances are, approximately, 2.11 and 2.37 Å in both cases. The average Co—(Cp) distance and the Co—(ring centroid) for II and III are 2.09 and 2.10, and 1.723 and 1.724 Å, respectively. Finally, the normal to the cyclopentadienyl ring makes angles of 89.64 and 89.91° with the normal to the plane of $Co(NO)_2Co$ and Co(CO)(NO)Co respectively. If the cyclopentadienyl ring is counted as a single ligand, the coordination around the cobalt atom is a distorted trigonal planar arrangement with one angle (X—Co—Y) of 99°. Precisely the same kind of arrangement prevails in $Cp_2Fe_2(NO)_2$ [3] and $Cp_2Co_2(CO)_2^-$ [8].

It is proper at this point to discuss the effect of the crystallographic disorder of CO and NO in $Cp_2Co_2(CO)(NO)$ (III) on the structural data presented here. From the fact that Bergman's [8] anion, $Cp_2Co(CO)_2^-$ (IV), has the same molecular dimensions as our (ordered) $Cp_2Co_2(NO)_2$ (II) derivative, one must conclude that the crystallographic disorder in no way causes problems in the accurate description of the structural parameters of III. In fact, since the metal—metal distances and the details of the structures of the bridging CO and NO groups seem to be the same, with negligible differences, we can now understand why compound III crystallizes so readily as disordered molecules. From this point on, we neglect completely the disorder in III, since we can point, further, that thermally speaking the crystals of III are better behaved than those of II.

The C_5H_5—Co fragment. So as to facilitate the discussion of the structural parameters of this fragment, we prepared Table 5 in which the various compounds entered are arranged in decreasing order of the Co—C(Cp) distance, the philosophy being that as this distance varies, we may see its effect on the other molecular parameters, or vice versa. The twelve compounds listed in Table 5 are easily divided into two classes; namely, those with sandwich arrangements of metal plus two hydrocarbons or metal plus hydrocarbon plus carborane. All these Co—(ring centroid) distances under 1.7 Å. The second class contains one cyclopentadienyl ring plus two bridging ligands opposite the C_5H_5 group. These have Cp—(ring centroid) distances longer than 1.7 Å, except in the case of XIV. Within one given class, the average Co—C(Cp) distance varies even though the Co—(ring centroid) distance is the same. For instance, take VII and XI with Co—C(Cp) distances ranging from 2.051(6) to 2.081(5) while the Cp C—C distances range from 1.426(8) to 1.402(9) (in VII) while in XI the Co—C(Cp) range from 2.042(3) to 2.057(4) and the Cp C—C distances from 1.373(6) to 1.408(6) Å. It is clear this is the result of ring vibrations, as demonstrated earlier [37—43].

As a result, discussion concerning variations in the individual Co—C(Cp) distances and in the C—C(Cp) distances is unproductive since all of these quantities are unreliable to different degrees. However, since the equations for the least squares planes are reliable in all cases [37—43], the variations in the Co—(ring centroid) distances are useful in gauging variations in bonding between the metal and the Cp rings. These vary according to the pattern described above, which is the same pattern one observes in going from ferrocenes to CpFeL

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TABLE 5

COMPARISON OF BONDING PARAMETERS FOR VARIOUS STRUCTURES CONTAINING THE (η^5-C_5H_5)Co FRAGMENT (The values listed are mean values and the numbers in parentheses are the deviations from the mean)

		Co—C (Å)	C—C (Å)	C—C—C (°)	M—Cp [a] (Å)	Reference
II	$(C_5H_5)_2Co_2(NO)_2$	2.101(12)	1.411(20)	108.2(10)	1.724	This study
III	$(C_5H_5)_2Co_2(CO)(NO)$	2.088(12)	1.388(8)	108.0(9)	1.723	This study
V	$C_5H_5CoC_7H_8N_2O_2$	2.081(9)	1.385(12)	108.0(7)	1.714	10
VI	$Cs[(C_5H_5)Co(CB_7H_8)]$-	2.074(9)	1.415(14)	108.0(9)	1.682	11
VII	2,6-$(C_5H_5)_2$-2,6-Co_2-	2.066(11)	1.417(10)	108.0(8)	1.682	12
	1,10-$(C_2B_6H_8)$	2.061(11)	1.413(8)	108.0(3)	1.674	
VIII	$[Et_4N][(C_5H_5)Co_2(C_2B_8H_{10})_2]$	2.064(8)	1.387(9)	108.0(8)	[c]	13
IX	$(C_5H_5)Co(6,7$-$C_2B_7H_{11})$	2.049(13)	1.407(2)	108(1)	[c]	14
X	$(C_5H_5)_2Co_2[$*trans*-$Ph_2C_4(thie)_2]$ [b]	2.056(4)	1.400(6)	108.0(10)	1.676	19
XI	$C_5H_5Co[C_4(C_6H_5)_2(SiMe_3)_2]$	2.049(7)	1.389(17)	108.0(9)	1.673	15
XII	$(C_5H_5)Co(C_2B_{10}H_{12})$	2.038(15)	1.405(14)	108(2)	1.651	16
XIII	$(C_5H_5)Co(C_4H_4)$	2.036(10)	1.390(6)	108.0(1)	1.660	17
XIV	$(C_5H_5)Co(S_2C_2(CN)_2]$	2.029(18)	1.402(23)	108(2)	1.642	18

[a] Metal ring centroid distance. [b] thie = 2-thienyl. [c] Information unavailable, equation of plane not given either.

TABLE 6

MOLECULAR PARAMETERS REPORTED FOR SPECIES OF THE TYPE $X\text{-}\mu\text{-}E^1O\text{-}\mu\text{-}E^2O\text{-}Y$ WITH X AND Y = METALS AND E^1 AND E^2 EITHER C OR N
(Distances in Å and angles in degrees. Only Co or Fe data listed here) [a, b]

	Compound	Reference	X	Y	E^1	E^2	Bond order [c]	X—Y	(X,Y)—E	E—O	E^1—(X,Y)—E^2	X—($E^{1,2}$)—Y	(X,Y)E—O
					Class A. Non-Planar [d] *derivatives*								
XV	$[(\eta^5\text{-}C_5H_5)NiCo(CO)_4(PEt_3)]$	20	Co	Ni	C	C	1	2,418(2)	1,929(10)	1,150(12)	87,3(4)	79,7(4)	139,3(9)
									1,928(10)	1,157(11)		79,3(4)	143,5(8)
XVI	$[(\eta^5\text{-}C_5H_5)NiCo(CO)_4(PR_3)]$	21	Co	Ni	C	C	1	2,425(2)	1,904(11)	1,176(12)	85,9(5)	79,4(4)	145,4(10)
	R = $p\text{-}FC_6H_4$								2,026(12)	1,145(14)		77,9(5)	138,0(11)
XVII	$[Co(\eta^4\text{-}CH_2\text{-}CMe)_2(CO)_2]_2$	22	Fe	Fe	C	C	1	2,510(1)	1,932(8)	1,170(9)	96,6(3)	81,2(3)	138,8(7)
									1,916(8)	1,177(9)	96,4(3)	81,5(3)	139,9(7)
									1,926(8)				139,0(7)
									1,928(8)				139,5(6)
XVIII	$[(\eta^4\text{-}Nbd)(OC)(Co\text{-}\mu_2\text{-}(CO)_2\text{-}$	23	Co	Fe	C	C	1	2,530(1)	1,905(4)	1,183(6)	95,1(2)	83,2(2)	136,6(4)
	$Fe(CO)(\eta^5\text{-}C_5H_5)]$								1,918(4)	1,175(6)		82,7(2)	135,5(4)
XIX	*cis*-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$	24	Fe	Fe	C	C	1	2,531(2)	1,908(7)	1,178(9)	96,0(3)	82,8(3)	137,8(6)
									1,925(7)	1,183(9)	96,0(3)	82,4(3)	139,4(6)
													139,2(6)
													138,4(6)
XX [e]	$(OC)_3Co\text{-}\mu_2\text{-}(CO)_2Co(CO)(Nbd)$	25	Co	Co	C	C	1	2,531(1)	1,867(4)	1,153(5)	91,1(2)	81,9(2)	142,0(4)
									1,875(4)	1,164(5)	84,5(1)	82,0(2)	141,3(4)
									1,993(5)				136,1(4)
									1,980(4)				136,1(4)

XXI[b]	$[(OC)_3Co\text{-}\mu_2\text{-}(CO)_2Fe(CO)(\eta^5\text{-}C_5H_5]$	26	Fe	Co	C	C	1	2,545	2,036(7) 1,882(7)	1,147(8)	87,5(3) 96,8(3)	80,9(3)	134,6(6) 144,5(6)
					Class B, Planar derivatives								
XXII	*trans*-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$	27	Fe	Fe	C	C	1	2,534(2)	1,910(5) 1,918(5)	1,188(6)	97,1(4)	82,9(2)	138,8(4) 138,4(4)
XXIII	$C_{16}H_{17}CoFeO_4$	28	Fe	Co	C	C	1	2,546(1)	1,966(7) 1,933(6)	1,160(8) 1,165(8)	95,7(3)	82,5(3) 82,8(3)	136,5(6) 138,0(5)
XXIV	$C_{16}H_{20}O_4Co_2$	29	Co	Co	C	C	1	2,549(1)	1,931(4)	1,155(5)	97,1(4)	82,9(2)	139,5(3) 137,6(3)
XXV	$C_{16}H_{16}O_4Co_2$	30	Co	Co	C	C	1	2,559(3)	1,911(10)	1,192(17)	95,8(6)	84,1(5)	138,0(3)
					Class C								
I	$(\eta^5\text{-}C_5H_5)_2Fe_2(NO)_2$	3	Fe	Fe	N	N	2	2,326(4)	1,768(9)	1,254(12)	97,7(4)	82,3(4)	138,8(8)
III	$(\eta^5\text{-}C_5H_5)_2Co_2(CO)(NO)$	this study	Co	Co	C	N	1,5	2,370(1)	1,829(7)	1,200(10)	99,3(2)	80,7(2)	139,4(3)
IV	$(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2^-$	8	Co	Co	C	C	1,5	2,372(2)	1,82(2)	1,21(4)	98,5(5)	81,2(5)	—
II	$(\eta^5\text{-}C_5H_5)_2Co_2(NO)_2$	this	Co	Co	N	N	1,0	2,372(1)	1,825(7)	1,188(10)	98,9(3)	81,1(3)	139,5(5)

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[a] Whenever a mixed Fe, Co compound occurs, only the Co information is listed. Nbd = norbornadiene. [b] When a Cp—metal fragment occurs with a metal bearing no Cp ring, only the data for the CpCo bearing fragment is given. In XX data for (Nbd)Co and $(OC)_3Co$ are given for emphasis; see footnote *e* and the Discussion. [c] Calculated according to the EAN rule. [d] Whenever relevant, the (Nbd)Co data are given first, followed by that for the $(OC)_3Co$ portion. [e] Entries on the upper half of each column belong to the Co atom of the (Nbd)Co fragment.

derivatives [44] (L = a suitable set of ligands such as $(CO)_2I$, $(CO)(PPh_3)Cl$, etc.). It is interesting to note, however, that there is no variation in the Co—(ring centroid) distance between II and III since the former has one electron more, and, consequently, a single Co—Co bond whereas the latter has, according to the EAN rule, a 1.5 order bond between the two metals.

The Co[μ_2-(CO)$_2$]Co fragment. A comment on the EAN rule. Briefly stated, the EAN rule says that a transition metal atom will combine with a set of donor ligands such that the total number of electrons (metal plus electrons donated by ligands) add to that of the nearest rare gas configuration. Thus, the metal has a total number of electrons equivalent to the number contained in the stable, rare gas, configuration. This rule is undoubtedly very useful, and it is generally obeyed. As such, it correctly predicts that certain fragments, such as $CpFe(CO)_2$, will be unstable unless they are (a) reduced to $CpFe(CO)_2^-$, (b) treated with a one-electron donor such as Cl^-, etc. to form $CpFe(CO)_2Cl$, etc., (c) allowed to dimerize to $Cp_2Fe_2(CO)_4$, in which case there is a two-electron (single) metal—metal bond. The argument is exactly that used to explain why the halide elements are diatomic. We have prepared Table 6 which shows that, for the general classes of compounds labelled class A and class B, this rule is not only obeyed but that the length of the metal—metal bonds remains very close despite the marked changes involved. Note that this observation is valid for both the *cis* and *trans* isomers, where relevant, and that changing from one isomer to the other changes the picture very little. The variations in metal—metal bond lengths can be explained, easily, by the variations in metal covalent radii (i.e., Fe vs. Co vs. Ni) and by the changes in ligands, which are quite drastic in some cases. Overall, the length of metal—metal bonds in class A compounds ranges from 2.418(2) to 2.559(3) Å, which amounts to a 6% change. It is equally true that the variations in the metal to bridging carbonyl (M—C) distance, the C—O distance and the angles of the entire fragments change very little, as well. Thus, the M[μ-(CO)$_2$]-M fragment seems to be largely invariant and it would appear that this rule can safely predict approximate values for the length of metal—metal bonds. As long as we are dealing with a single metal—metal bond (class A compounds) the expectation is that the bond length of M—M′ should be about 2.5 Å, irrespective of the nature of M and/or M′ (M, M′ = Fe, Co or Ni) (Table 6).

Recently, Calderon et al. [3] studied the structure of $Cp_2Fe_2(NO)_2$ (I) and found, according to the EAN rule prediction, that there is a short Fe—Fe distance of 2.326(4) Å, which was readily explained on the basis that a compound with that composition should have a four electron (double bond) between the two iron atoms. Comparison of their result with those of Bergman et al. [8] for $Cp_2Co_2(CO)_2^-$ (IV has a 1.5 bond order between Co atoms, according to the EAN rule), our study of $Cp_2Co_2(CO)(NO)$ (III) which is isoelectronic with IV and, most importantly, with $Cp_2Co_2(NO)_2$ (II), which should have a single Co—Co bond, show that the metal to metal bonds are of nearly the same length in all four cases. It is important to stress, that not only are I, II, III, and IV molecularly identical (see Table 6, class C for details of the molecular parameters) but, more important, I, II and III are isomorphous and isostructural. Therefore, all crystallographic effects are identical for these three species. Further, according to Pauling [44], the difference in radii between Fe and Co is 0.01 Å. This difference, if used, would predict a larger Co—Co distance for the same bond order. However, the point is that the EAN rule predicts a single bond for II and a double bond for I.

We must conclude at this point that the EAN rule is unreliable as a criterion for predicting finer details such as bond orders and bond lengths. The bonding details (Table 6) for I, II, III and IV demonstrate this point amply. Early in our search of the literature, we were struck by the homogeneity of the values for metal—metal bonds for compounds in class A and class B and attributed the change in metal—metal bond between the isoelectronic species III and IV and those compounds of class A and B to a change in bond order. In fact, our carbonylnitrosyl (III) and Bergman's anion (IV) are predicted to have a 1.5 Co—Co bond order. However, we then determined the structure of the dinitrosyl (II) and found the result of Calderon et al. [3], and realized that this was not a valid explanation for these results. Finally, we must comment that the differences in metal—metal bond lengths observed for classes A and B, on the one hand, and those on class C cannot be simply explained on a change in structure because (a) there are equally drastic structural changes within the compounds of classes A and B, (b) the compounds in class C have the identical same structure and bonding parameters and for them the EAN rule would predict a smooth increase in metal—metal bond length from I to (III and IV) to II. In conclusion, when we go from $Cp_2Co_2(NO)_2$ to either $Cp_2Co_2(CO)(NO)$ or its isoelectronic anions $Cp_2Co_2(CO)_2^-$ and, finally, to $Cp_2Fe_2(NO)_2$ the successive increase in bond order predicted by the EAN rule is not observed. The implication is that the electrons associated with these changes must come from orbitals which are non-bonding in character, as far as the dinuclear metal framework is concerned. Our research is directed currently to probe further into this interesting question.

The ESR spectrum of $Cp_2Co_2(NO)(CO)$

Given the composition of this substance, one expects it to be paramagnetic ($S = 1/2$). In fact, this had been recently demonstrated by Müller and Schmitt [5] who measured its magnetic moment (1.86 BM) compound III is isoelectronic with the anion IV as shown by ESR spectroscopy [8]. As a fine tool for probing electron distribution and because it seemed desirable to compare III and IV, we recorded the ESR spectrum of III. The results are shown in Fig. 3 where it is clear that there are 15 lines having relative intensity ratios of approximately 1/2/3/···7/8/7···3/2/1. This is, of course, a classic pattern already found in $[(H_3N)_5CoOOCo(NH_3)_5]^{5+}$ [31,32] and in IV [8], and is associated with an unpaired electron equally delocalized over two ^{59}Co nuclei ($I = 7/2$; abundance ca. 100%). It is also clear that there is no evidence of further splitting by the N nucleus of the nitrosyl bridge. One must, however, note that while the splitting due to the Co nuclei is 47.4 Oe, the linewidth is ca. 29 Oe. In order to place these numbers in perspective, we have prepared Table 7 in which a number of ESR spectral parameters of relevant molecules are listed.

From these data, the parameters of the ESR spectra of III and IV are the same, to the accuracy quoted. This is not very surprising since the structural parameters in III and IV are essentially identical. In particular, note that the Co—Co, Co—N or Co—C distances are identical within stated accuracy. Therefore, one expects the unpaired electron to be distributed, approximately, equally in the two substances. This is an interesting observation which agrees well

TABLE 7

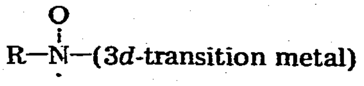
COMPARISON OF ESR PARAMETERS WITH SOME RELEVANT VALUES FROM THE LITERATURE (Hyperfine splittings are given in Oe)

Compound		a(Co)	a(N)	g-factor	Reference
III	$(\eta^5\text{-}C_5H_5)_2Co_2(NO)(CO)$	47.4	14 [a]	2.0539	This reference
IV	$(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2^-$	ca. 50	—	2.091	8
XXV	$\mu_3\text{-}RCCo_3(CO)_9^-$	ca. 35	—	Not given	33
XXVI	$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4N(=O)\text{-t-}C_4H_9)Fe$	—	11.75	2.0149	34
XXVII	$C_6H_5N(=O)\text{-t-}C_4H_9$	—	12	2.006	35
XXVIII	$[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$	12.7	—	2.037	31,32
XXIX	$CF_3(NO)Co(CN)_5$	10.25	13.92	2.0066	36
XXX	$CF_3(NO)Co(DMG)$ [b]	10.1	13.6	2.0065	36

[a] Estimated value from linewidths. See text. [b] DMG = dimethylglyoximato.

with the commonly accepted idea that in organometallics the change from one group (effectively CO^- for NO) having the same number of electrons to contribute to the bonding, results in the same total electronic distribution around the core atom. We note, next, that the spectroscopic splitting factor for III is $g = 2.0539$, which is higher than 2.0023 (the free electron value) by a significant amount. This is expected for a transition element compound of the $3d$ series due to the spin-orbit contribution; it is also in accord with the measured value of the magnetic moment for III given by Müller and Schmitt [5] which is larger than the value of 1.73 BM expected for a free electron. The fact that the g factor for III exceeds the free radical value implies a negative value for the spin-orbit coupling constant, which is to be expected of any cobalt compound whose effective charge is less than 5+ and which is certainly the case for III and IV, no matter how electrons are counted.

Concerning the magnitude of the ^{14}N hyperfine constant, the results quoted in Table 7 show that for a relevant number of compounds having the fragment:



$$R{-}\underset{\bullet}{\overset{\overset{\textstyle O}{|}}{N}}{-}(3d\text{-transition metal})$$

it does not exceed 12—14 Oe [34—36]. These substances have g values that are consistent with their formulation as "free radical-like" and contain an unpaired electron which can be labelled as "ligand based". The ^{59}Co hyperfine splitting constant for these substances is approximately 1/4 those observed for III and IV. Also, note that they are approximately the same as those observed in μ-peroxodecaaminodicobalt [31,32] for which Weil and Kinnaird [32] estimate that the unpaired electron spends 90% of the time on the O_2 bridge. Thus, it is quite likely that the ^{14}N splitting is lost in the 29 Oe linewidth, whose large value may be due to stereochemical non-rigidity and/or solvent perturbations in the open Co—(bridge)—Co fragment. A careful study of the line shapes as a function of temperature may still reveal the magnitude of the ^{14}N interaction; until such time, nothing definite can be said about the path of the unpaired electron in moving between the two cobalt atoms over which it is delocalized. At the moment we only can, on the basis of linewidths, assign an upper limit of 12—14 Oe to the ^{14}N hyperfine splitting. Concerning the ^{59}Co anions (XXV)

TABLE 8

SPECTRAL, ANALYTICAL, AND POLAROGRAPHIC DATA

Mass spectrum (Direct inlet T_E 10°C; T_Q *150°C*; P 70 eV): Parent ion M^+ at m/e 306 (rel. int. 14%), $[M-CO]^+$ (278; 2%), $(C_5H_5)_2Co^+$ (189, 100%), $C_5H_5Co^+$ (124, 34%), Co^+ (59, 15%), m^* 116.7 (broad, very intense) corresponds to the decay process 306 → 189.

IR (KBr): 1545 cm^{-1} (ν(NO)); 1819 cm^{-1} (ν(CO)).

Analytical data: Found: C, 43.25; H, 3.59; N, 4.50; Co, 37.09; mol. weight, 345 (osmometrically in benzene). $C_{11}H_{10}Co_2NO_2$ calcd.: C, 43.17; H, 3.29; N, 4.58; Co, 38.51%; mol. weight 306.07. The compound has no melting point up to 250°C, but decomposition starts out slowly at ca. 90°C and is complete at ca. 160°C (lit. [5] m.p. 124°C (decomp.)).

Cyclic voltammetry (Solvent: acetonitrile, supporting electrolyte: $(n\text{-}Bu_4N)ClO_4$ [conc. 5×10^{-2} *M*]; reference electrode: SCE; sample concentration: 5×10^{-4} *M* in both cases; platinum wire electrode; +25°C; d.c. measurements; scanning rate: 200 mV/sec; Electrochemical system, Model 170 [Princeton Applied Research Company]): Compound II: reduction $E_{1/2}$ = (—1.13 V; irrev.); oxidation (+0.29 V, rev.) Compound III: reduction (—1.10 V; rev.); oxidation (—0.28 V; rev.).

reported by Kotz et al. [33], we see that both the *g* factors and the hyperfine splittings, consistently, point to these species as having a more "metal based" unpaired electron than the other entries of Table 7. Using Weil and Kinnaird's [32] estimate of ca. 10% for the distribution of the unpaired electron over the two ^{59}Co nuclei of $[(H_3N)_5Co{-}O_2{-}Co(NH_3)_5]^{5+}$ and assuming a roughly linear change, the unpaired electron spends about 40% of the time on the metals of III. Finally, we want to call the reader's attention to the fact that in the anions of Kotz et al. [33] there are three cobalt atoms and that the ^{59}Co splitting is ca. 2/3 the value found in either III or IV. Since the sum of the individual spin densities at all atoms of a species with spin 1/2 must addd to unity, the obvious conclusion is that for III, IV, and XXV, the fraction of the time the unpair electron spends on the metal framework and on the bridging framework are about the same.

Electrochemistry of II and III

The electrochemical processes described by the data of Table 8 indicate that the dinitrosyl derivative II can easily be oxidized to its cation, $Cp_2Cp_2(NO)_2^+$, which would be isoelectronic with the known, stable, species III and IV. Consequently, it is not surprising to find that this is a reversible process. The same comments can be made about the reduction of III to $Cp_2Co_2(CO)(NO)^-$. Oxidation of III to its cation and reduction of II to its anion are both irreversible processes and would correspond to the formation of $Cp_2Co_2(CO)(NO)^+$ and $Cp_2Co_2(NO)_2^-$, respectively. The former, III$^+$, would be isoelectronic with $Cp_2Co_2(CO)_2$ which has been isolated recently [1]. The anion, II$^-$, probably undergoes a bridge splitting reduction similar with those known to occur in species of the type $Cp_2Fe_2(CO)_4$ and $Cp_2Mo_2(CO)_6$, etc. Our observations for II and III parallel the recent experiences described by Bergman and associates with $Cp_2Co_2(CO)_2^-$ [7,8].

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