THE CRYSTAL AND MOLECULAR STRUCTURE OF BICYCLO[2 2 1]-HEPT-2-EN-5,6-DINITROSOCOBALT-η^5-CYCLOPENTADIENIDE. EVIDENCE FOR A NITROXYL DIRADICAL BIDENTATE LIGAND

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Summary

An accurate X-ray crystallographic structural study of a metal complex having a nitroxyl diradical as a bidentate ligand has been carried out Bicyclo[2 2 1]-hept-2-en-5,6-dinitrosocobalt-η^5-cyclopentadienide crystallizes in space group $P\bar{1}$ with Z 2, a 8 245 ± 0 007, b 10 285 ± 0 016, c 7 888 ± 0 008 Å and α 59 276 ± 0 073, β 101 099 ± 0 053, γ 108 802 ± 0 067° Intensities of 1831 independent reflections were used in the refinement of the structure to an $R(F)$ of 4 6% The bonding of the Co atom to the cyclopentadienyl ligand appears to be a normal pentahapto linkage The lone double bond and the C—C single bonds adjacent to the endo hydrogens of the norbornene fragment of the molecule are shorter than have previously been reported for this moiety This study represents the first structural report of NO groups bridging to Co. The Co—N—O angles (129.4(3) and 128.9(3)°) and the NO stretching frequency (1357 cm^{-1}) of the title compound resemble values found in nitroxyl free radical compounds more closely than values found in bridging NO group compounds

Introduction

In 1971, Brunner and Loskot [1] reported the reactions of olefins with organo cobalt compounds in the presence of NO. In particular, they reported that the reaction of [$(\eta^5$-C$_5$H$_5$)Co(CO)$_2$] with the Diels—Alder adduct of cyclopentadiene and the dimethyl ester of acetylenedicarboxylic acid, in the presence of NO, gives an unusual compound to which they assigned the following chemical com-

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position and structure

R = COOCH₃

(I)
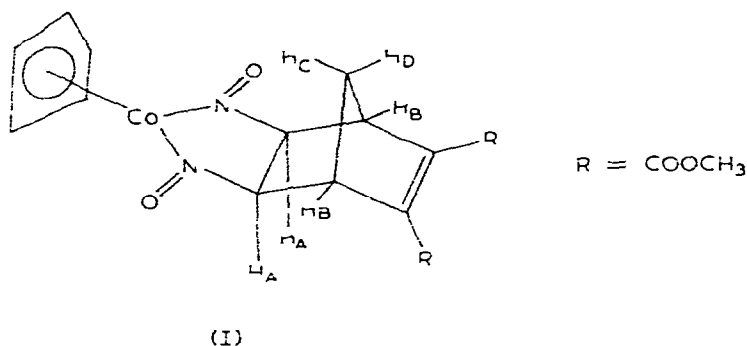
The existence of bridging NO groups was inferred from the value of the NO stretching frequency (1357 cm⁻¹) and the *endo* configuration of the hydrogens (H_A) at positions 5 and 6 was assigned on the basis of H-NMR arguments Since this molecule is unique in composition and the configurational assignments needed to be verified, we undertook an X-ray diffraction study of the crystal and molecular structure of the substance in the form of the parent compound (I, R = H) Our results verify all compositional, conformational and configurational assignments made by Brunner and Loskot [1]. Furthermore, this is the first study of a μ-nitroso cobalt compound and one of the few studies available of either an *ortho*-dinitroso organic compound or of a norbornene fragment (vide infra)

Experimental

A fairly well-shaped dark, almost black, single crystal suitable for X-ray diffraction studies was selected from material kindly supplied by Professor Henri Brunner The crystal was approximately a parallelepiped in shape It was bounded by six faces of the following forms and indices {100}, {001}, (13̄2̄) and (1̄31̄). Perpendicular distances from an origin chosen at the intersection of three faces, the (1̄00), (001̄) and (13̄2̄), to the remaining faces were as follows. 0 20 mm to the (100), 0 17 mm to the (001), and 0 30 mm to the (1̄31̄). The volume of the data crystal was 0 01978 mm³.

Preliminary Weissenberg and precession X-ray photographs established that the crystal is triclinic. The assumption that it is centrosymmetric, so that the space group is P1̄, has been proved correct by the structural analysis. Approximate unit-cell dimensions were refined by least-squares analysis using observed diffractometer data for twenty-four reflections, automatically centered under computer control. The crystal data are summarized in Table 1.

Using graphite monochromatized Mo-K_α X-radiation (λ = 0 71069 Å), intensity data were collected under computer control using the Brookhaven Multiple Spectrometer Control System [2]. The $\theta - 2\theta$ step-scan technique was used with the scan length determined by the function $\Delta 2\theta = 2.0° (1 + 0.7 \tan \theta)$. The step size was chosen to give approximately 50 points in each scan. Data were collected out to sin θ/λ = 0.649 Å⁻¹ and included measurements of many

TABLE 1

CRYSTAL DATA $C_{12}H_{13}N_2O_2Co$ f w 276 18 Space Group $P\bar{1}$ triclinic

a	8 245 ± 0 007 Å	α	59 276 ± 0 073°
b	10 285 ± 0 016	β	101 099 ± 0 053
c	7 888 ± 0 008	γ	108 802 ± 0 067
v	544 01 Å³ Z 2		
d_{meas}	1 690 gms cm⁻³		
d_{calc}	1 686 gms cm⁻³		
μ	16 227 cm⁻¹		

Range of transmission coefficients calculated 0 73 to 0 79

reflections in both hemispheres of reciprocal space The total of 3282 integrated intensity measurements yielded a unique data set of 1831 observed intensities with $I > 3 \sigma (I)$ I is the background corrected integrated intensity and $\sigma(I)$ its e.s d based on counting statistics Two standard reflections were measured at regular intervals to monitor the crystal and electronic stability No corrective measures were required by the observed variations

Background corrections were made using a method [3] which separates the peak and background in such a way that $\sigma (I)/I$ is minimized Lorentz, polarization and absorption corrections were applied to the data Polarization due to the pyrolytic graphite monochromator crystal was neglected The Gaussian integration method [4] with a grid of 512 points was used in the absorption correction calculations, where the crystal shape was represented by the six rational boundary planes described above

Structure solution and refinement

A three-dimensional sharpened Patterson map showed the position of the Co atom in the unit cell Subsequently, all other atoms in the molecule were revealed by Fourier and difference Fourier maps

The full-matrix least-squares refinement of the structure proceeded in a straightforward manner. $R' = \Sigma w(|F_0| - |F_c|)^2$ was the quantity minimized, where F_0 and F_c, respectively, are the observed and calculated structure amplitudes and $w = 1/\sigma^2(F_0)$ is the weight for each reflection. $\sigma(F_0)$ was given by $\sigma(F_0) = (\sigma^2(F_0) + (0\ 075|F_0|)^2)^{1/2}$ with $\sigma^2(F_0)$ based only on counting statistics All 1831 observed reflections were included in each refinement cycle In the final cycle, a single scale factor, the atomic positions and the anisotropic thermal parameters for all non-hydrogen atoms were varied All hydrogen atoms were found in the difference Fourier maps and their contributions were included in the least-squares cycles, but their positional and isotropic thermal parameters were not varied Ultimately the hydrogen atom positions were idealized. The C—H distances were set to 0.97 Å and the isotropic temperature factors were set to 4 4 Å²

The final R-factors for the refinement were $R_1 = \Sigma|F_0| - kF_c|/\Sigma|F_0| = 4\ 6\%$ and $R_2 = [\Sigma w(F_0 - kF_c)^2]^{1/2}/(\Sigma w F_0^2)^{1/2} = 5.9\%$. The error in an observation of unit weight was as follows: Error $= [\Sigma w(F_0 - kF_c)^2/(m - n)]^{1/2} = 1.23$ where m = total number of observations and n = total number of parameters varied. Throughout the refinement calculations, the atomic scattering curves of Cromer

TABLE 2

POSITIONAL PARAMETERS

Atom	x/a	y/b	z/c
Co	−0 17711(6)	0 22754(6)	−0 18173(7)
O1	−0 2524(4)	0 1675(4)	0.1782(4)
O2	0 1172(4)	0 2333(4)	−0 2976(4)
N1	−0.1493(4)	0 1828(4)	0 0675(4)
N2	0 0353(4)	0 2184(4)	−0 1684(5)
C1	0 1363(5)	0 1878(4)	0 0197(5)
C2	0 0194(5)	0 1593(4)	0 1694(5)
C3	0 1145(5)	0 2878(5)	0 2287(6)
C4	0 1821(5)	0 4244(5)	0 0280(6)
C5	0.2819(5)	0 3338(5)	0 0021(6)
C6	0 3777(5)	0 2744(6)	0 1992(7)
C7	0 2788(6)	0 2467(6)	0 3325(6)
CC1	−0 2331(7)	0 3522(7)	−0 4811(7)
CC2	−0 2940(7)	0.1933(7)	−0 4201(7)
CC3	−0 4128(6)	0.1295(6)	−0 2794(8)
CC4	−0 4259(7)	0 2480(8)	−0 2506(8)
CC5	−0 3152(8)	0 3886(6)	−0 3806(9)

[5a] were used The curve for Co included corrections for anomalous dispersion [5b].

Tables 2, 3, and 4, respectively, list the atomic position parameters, anisotropic temperature factors and idealized hydrogen atom positions * Bond lengths and angles are listed in Tables 5 and 6, respectively

TABLE 3

THERMAL PARAMETERS (×10^4) ^{a}

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	74 8(9)	85 7(8)	95 7(11)	21.5(6)	−11.7(6)	−45 4(7)
O1	90(5)	180(6)	155(7)	17(4)	29(5)	−96(5)
O2	121(5)	199(6)	173(8)	52(5)	14(5)	−124(6)
N1	68(5)	93(5)	99(7)	5(4)	8(4)	−46(5)
N2	90(5)	79(5)	113(7)	19(4)	5(5)	−53(5)
C1	77(6)	76(5)	119(8)	30(4)	−8(5)	−50(5)
C2	82(6)	76(5)	84(7)	11(4)	1(5)	−31(5)
C3	94(6)	112(6)	122(9)	26(5)	−15(6)	−74(6)
C4	93(6)	83(6)	165(9)	18(5)	−2(6)	−66(6)
C5	76(6)	96(6)	142(9)	17(5)	2(6)	−65(6)
C6	92(7)	140(7)	210(11)	49(6)	−54(7)	−106(8)
C7	120(7)	139(7)	157(10)	36(6)	−52(7)	−89(7)
CC1	151(9)	195(10)	105(10)	39(8)	−31(7)	−23(8)
CC2	161(9)	209(10)	202(12)	85(8)	−85(8)	−151(10)
CC3	106(8)	126(8)	235(13)	0(6)	−79(8)	−61(8)
CC4	142(9)	316(14)	184(12)	142(10)	−73(8)	−152(11)
CC5	238(12)	134(8)	268(15)	113(8)	−156(11)	−115(10)

^{a} Anisotropic temperature factors of the form. $T_i = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

TABLE 4

IDEALIZED HYDROGEN POSITIONS [a]

Atom	x/a	y/b	z/c
HC1	0 183	0 101	0 056
HC2	−0 003	0 055	0 283
HC3	0 047	0 303	0 303
HC4 1	0 092	0 454	−0 073
HC4 2	0 255	0 517	0 034
HC5	0 351	0 388	−0.113
HC6	0 492	0 259	0.223
HC7	0 307	0 208	0 472
HCC1	−0 146	0 426	−0 579
HCC2	−0 258	0 137	−0 468
HCC3	−0 477	0 020	−0 211
HCC4	−0 498	0 236	−0.157
HCC5	−0 299	0 493	−0 398

[a] All hydrogen atoms were assigned an isotropic thermal parameter of 4 4 $Å^2$ The C—H distance in all cases was 0 97 A Each hydrogen atom is labelled according to the carbon atom to which it is attached

TABLE 5

BOND DISTANCES (A)

Co—CC1	2 074(5)	CC1—CC2	1 384(8)
Co—CC2	2 085(4)	CC2—CC3	1 372(7)
Co—CC3	2 084(4)	CC3—CC4	1 388(8)
Co—CC4	2 069(5)	CC4—CC5	1 403(9)
Co—CC5	2.092(5)	CC5—CC1	1 379(8)
Co—cen [a]	1 714(5)		
Co—N1	1 761(3)		
Co—N2	1.764(3)		
N1—O1	1 252(4)		
N2—O2	1 247(4)		
N1—C2	1.492(5)		
N2—C1	1 487(5)		
C1—C2	1 520(5)		
C1—C5	1.551(5)		
C2—C3	1 550(5)		
C3—C4	1.534(6)		
C3—C7	1 507(6)		
C4—C5	1 530(5)		
C5—C6	1 511(6)		
C6—C7	1 314(7)		

[a] cen ≡ center of cyclopentadienyl ring.
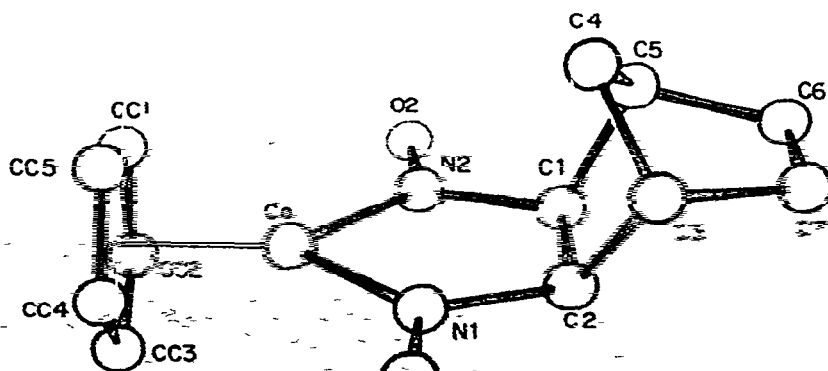
TABLE 6

BOND ANGLES (Deg)

N1—Co—N2	87 6(1)		
Co—N1—O1	129 4(3)	C1—C5—C4	100 7(3)
Co—N1—C2	118 2(2)	C1—C5—C6	104 0(3)
O1—N1—C2	112 4(3)	C4—C5—C6	100 2(3)
Co—N2—O2	128 9(3)		
Co—N2—C1	118 2(2)	C5—C6—C7	107 8(4)
O2—N2—C1	112 9(3)	C3—C7—C6	107 7(4)
N2—C1—C2	108 0(3)	CC5—CC1—CC2	108 9(5)
N2—C1—C5	112 4(3)	CC1—CC2—CC3	108 0(5)
C2—C1—C5	103 6(3)	CC2—CC3—CC4	108 4(5)
		CC3—CC4—CC5	107 7(5)
N1—C2—C1	107 9(3)	CC4—CC5—CC1	107 1(5)
N1—C2—C3	111 7(3)		
C1—C2—C3	103 0(3)		
C2—C3—C4	100.1(3)		
C2—C3—C7	105 5(3)		
C4—C3—C7	100 4(3)		
C3—C4—C5	93 6(3)		
cen [a]—Co—N1	137 7(3)		
cen—Co—N2	134 7(3)		

[a] cen = center of cyclopentadienyl ring.

Description of the molecular structure and discussion

Fig 1 shows the shape of the molecule and the atom numbering system used in the crystallographic study.

Fig 2, a stereographic view depicting the molecule in the same orientation as in Fig. 1, shows that the molecule indeed contains a pair of *endo* hydrogens at positions 5 and 6 and that the cobalt atom is bridged by a pair of NO fragments to the *exo*-5,6 positions of the norbornene In the following, we present a quantitative discussion of the molecular bonding parameters of the various fragments of the molecule

A The $(\eta^5-C_5H_5)Co$ fragment

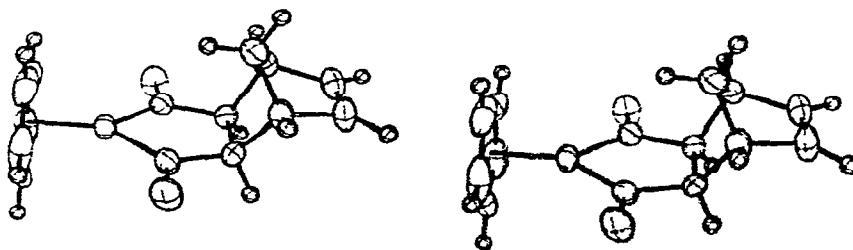The bonding of the Co atom to the five carbons of the cyclopentadienyl lig-

Fig 2 A stereographic view of the molecule showing the thermal motion of the atoms as 50% probability ellipsoids and showing the hydrogen atoms in their proper (idealized) positions

and is that expected for a normal pentahapto linkage As can be seen from the data in Table 5, the range of values for the Co—C bonds is narrow (2 069(5) to 2 092(5) Å) and the difference between extreme values (0 023 Å) is, perhaps, just barely significant (3 2 σ) Any significance of this difference is diminished even further when viewed against the deviations of the carbon atoms of the cyclo pentadienyl group from the best plane through them, as determined by least squares The deviations range from +0 009 Å to —0 011 Å for CC4 and CC5, respectively, the same two carbon atoms as are involved in the extreme Co—C distances A comparison of our results with others obtained from recent literature reports is given in Table 7, where one can see that there is a range of mean values from 2 029(18) to 2 081(9) Å and that their difference (0 052 Å) is again barely significant (2 58 σ) In all cases listed in Table 7, the rings are planar and, therefore, have average internal C—C—C angles of 108° as expected for a pentagon The values of the C—C distances range from 1 385(12) to 1 417(10) Å but there seems to be no correlation between the variations in C—C distances and those in the Co—C distances In fact, the difference between the extreme values for the C—C distances (0 032 Å) is just barely significant (2 05 σ) while the difference between the C—C distances in compounds I and IX, which are sterically closely related, is only 0 017 Å which is certainly not significant (0 66 σ)

B The norbornene fragment

Beside this study of the norbornene moiety, there are only six others in the structural literature [14—16,24—26] Of these, three [14,24,26] contain norbornene fragments which are a part of larger fused systems. Furthermore, the errors associated with the bond lengths and angles in three of these studies [24—26] are quite large (e s d 's on lengths = 0 018—0 030 Å, e.s d.'s on angles = 1 2—2 0°). Therefore, they are not suitable for comparison with our results However, generally they are in good agreement with the results shown in Table 8. We have included in Table 8 the more accurate results for the polycyclic systems [16] which are available and, for comparison, the results of the electron diffraction study of norbornadiene by Muecke and Davis [17] The skeletons which resemble the title compound most are those of compounds X and XI, which are shown below together with that of XII

TABLE 7

COMPARISON OF BONDING PARAMETERS FOR VARIOUS STRUCTURES CONTAINING THE $(\eta^5\text{-}C_5H_5)Co$ FRAGMENT THE VALUES LISTED BELOW ARE MEAN VALUES AND THE NUMBERS IN PARENTHESES ARE THE DEVIATIONS FROM THE MEAN

	Compound	Co—C (Å)	C—C (Å)	C—C—C (°)	Reference
I	$C_5H_5CoC_7H_8N_2O_2$	2 081(9)	1 385(12)	108 0(7)	this study
II	$Cs[(C_5H_5)Co(CB_7H_8)]$	2 074(9)	1 415(14)	108 0(9)	6
III	$2,6\text{-}(C_5H_5)_2\text{-}2,6\text{-}Co_2\text{-}1\ 10\text{-}(C_2B_6H_8)$	2.066(11)	1 417(10)	108 0(8)	7
		2.061(11)	1 413(8)	108 0(3)	
IV	$[Et_4N][(C_5H_5)Co_2(C_2B_8H_{10})_2]$	2 064(8)	1 387(9)	108 0(8)	8
V	$(C_5H_5)Co(6,7\text{-}C_2B_7H_{11})$	2 049(13)	1.407(2)	108(1)	9
VI	$(C_5H_5)Co[C_4(C_6H_5)_2(SiMe_3)_2]$	2 049(7)	1 389(17)	108 0(9)	10
VII	$(C_5H_5)Co(C_2B_{10}H_{12})$	2 038(15)	1.405(14)	108(2)	11
VIII	$(C_5H_5)Co(C_4H_4)$	2.036(10)	1.390(6)	108.0(1)	12
IX	$(C_5H_5)Co[S_2C_2(CN)_2]$	2.029(18)	1 402(23)	108(2)	13

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TABLE 8

COMPARISON OF BOND LENGTHS (Å) AND ANGLES (°) WITHIN THE NORBORNENE FRAC OF THE TITLE COMPOUND WITH RELEVANT DATA AVAILABLE IN THE CHEMICAL LITERATURE Bond lengths and angles of chemically equivalent fragments are tabulated Atom lat those used in the present crystallographic study Reference should be made to Fig 1 if necessary
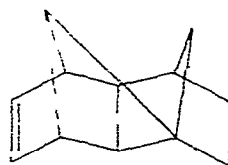
Compound		C3—C7 and C5—C6	C7—C6	C1—C5 and C2—C3	C3—C4 and C4—C5	C1—
I	$(C_5H_5)Co(C_7H_8N_2O_2)$	1 507(6) 1 511(6)	1 314(7)	1 551(5) 1 550(5)	1 534(6) 1 530(5)	1 52
X	$C_{33}H_{25}N_3O_3$ (exo)	1 524(14) 1 541(15)	1 356(16)	1 622(11) 1 585(15)	1 469(17) 1 508(13)	1 61
XI	$C_9H_8O_3$ (endo)	1 513(7) 1 515(7)	1 350(7)	1 566(7) 1 585(7)	1 565(7) 1 547(7)	1 54
XII	$C_{12}H_8Cl_6$ (exo)	1 513(7) 1 518(6)	1 361(7)	1 580(6) 1 583(6)	1 543(6) 1 583(6)	1 60
XIII	Norbornadiene (C_7H_8)	1 549	1 357	—	1 568	—
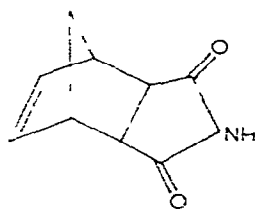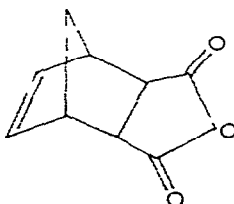
(X)   (XI)   (XII)

The length of the double bond (C7—C6) in the title compound I is shorter than that found for compounds X, XI and XII, the difference being 2 40 σ, 3 64 σ, and 4 75 σ, respectively Assuming that the e.s d of the (C7-C6) bond length measurement in the electron diffraction study is no worse than that for compound X (0 016 Å), it too differs from I to a level of significance of 2 46 σ At the same time, and to different levels of significance, the length of the single bond (C1—C2) at the fusion point with the five-membered ring is also shorter in I than in all the others. Finally, the lengths of both single bonds (C1—C5 and C2—C3) are shorter in I than in the other compounds These are the only general trends which are apparent in the data of Table 8. For example, the important angle at C4, the bridgehead carbon, is identical in I and XI and smaller than in all the other compounds, including norbornadiene. This result is interesting since the configuration at C1 and C2 in I is *endo* with respect to the hydrogens HC1 and HC2 and *exo* with respect to the atoms of the fused five-membered ring The opposite is true in XI. Yet the angle at the bridgehead carbon is larger in X than in XI, where the configuration at C1 and C2 is the same. Along the same lines, one notes that the angles C2—C3—C7 and C1—C5—C6 in I are about the same as those in X but smaller than in the other compounds. Thus, we are forced to conclude that, at this stage, no general trend is apparent for the distances and

C1—C2—C3 C2—C1—C5	C5—C6—C7 C3—C7—C6	C2—C3—C7 C1—C5—C6	C1—C5—C4 C2—C3—C4	C4—C5—C6 C4—C3—C7	C3—C4—C5	Reference
103 0(3) 103 6(3)	107 8(4) 107 7(4)	105 5(3) 104 0(3)	100 7(3) 100.1(3)	100 2(3) 100 4(3)	93 6(3)	this study
100 8(8) 102 5(6)	106 4(9) 108 0(9)	105 0(7) 105 2(9)	98 4(9) 98 5(7)	99 6(7) 102 1(9)	99 0(8)	14
103 3(5) 103 2(5)	107 6(5) 107 6(5)	108 1(5) 106 5(5)	97 7(5) 98 3(5)	101 3(5) 101 0(5)	93 5(5)	15
104.9(3) 100 4(3)	107 2(4) 108 9(4)	109 7(3) 107 2(3)	93 0(3) 101 6(3)	103 2(4) 101 6(3)	94 7(3)	16
—	108 5	106 6	—	95 9	96 2	17

angles of the norbornene fragments (molecules) so far studied The same situation exists in the case of the norbornane moiety, as has been carefully documented by Sundaralingam and associates [27] However, as a result of the high degree of internal self-consistency, particularly in bond lengths, we feel confident that our description of the norbornene moiety is highly reliable

C The $CoN_2O_2C_2$ fragment

This fragment is interesting because, so far, there are no descriptions in the structural literature for μ-nitroso cobalt derivatives Furthermore, little is known about *ortho* dinitroso organic compounds except for the study by Cady, et al. [19] of hexanitrosobenzene, which turned out to be benzotrifuroxan Thus, the molecule contains three five-membered rings (CCNON) fused to the phenyl ring, as shown below XV Note the existence of NO groups acting as bridges to a C and an O
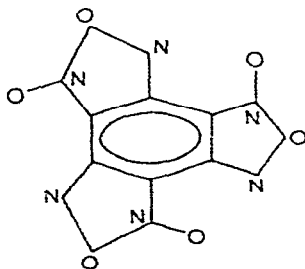
(XV)

A pair of NO bridged iron compounds and three nitroxyl free radicals were also found in the structural literature. The structural results for these are presented
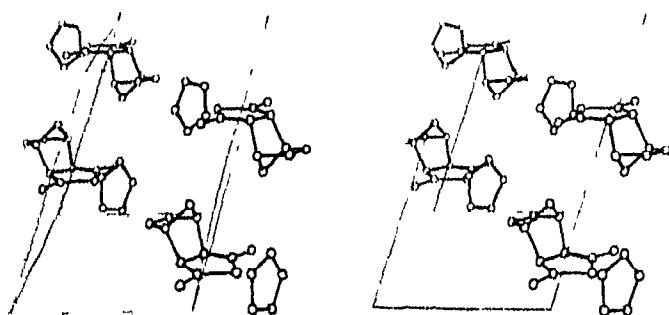
Fig 3 A stereographic packing diagram for the structure

TABLE 9

BOND LENGTHS (Å) AND ANGLES (°) OF THE $CoN_2O_2C_2$ FRAGMENT AND COMPARISONS WITH RELEVANT DATA AVAILABLE IN THE LITERATURE
Bridging NO fragments are bonded to two atoms, X and Y

	Compound	X	Y	X—N	Y—N	N—O	X—N—O	Y—N—O	X—N—Y	Reference
I	$(C_5H_5)Co(C_7H_8N_2O_2)$	Co	C	1 761(3)	1 492(5)	1 252(4)	129 4(3)	112 4(3)	118 2(2)	this
				1 764(3)	1 487(5)	1 247(4)	128 9(3)	112 9(3)	118 2(2)	study
XIV	$(C_5H_5)_2Fe_2(NO)_2$	Fe	Fe	1 768(9)	1 768(9)	1 254(12)	138 8(8)	138 8(8)	82 3(4)	18
XV	$C_6(NO)_6$	C	O	1 329(12)[a]	1 476(9)[b]	1 206(5)[b]	135 5(6)[b]	118 8(5)[b]	105 7(3)[b]	19
XVI	$[(FeL)_2NO]PF_6$[c]	Fe	Fe	1 818(5)	1 818(5)	1 193(8)	137 2(1)	137 2(1)	85 5(3)	20
XVII	$C_9H_{15}N_2O_2$[d]	C	C	1 477(7)	1 486(6)	1 267(5)	123 0(5)	122 2(5)	114 8(5)	21
XVIII	$C_{26}H_{46}N_2O_6$[e]	C	C	1 487(8)	1 495(5)	1 276(5)	116 4(5)	116 6(5)	123 9(5)	22
XIX	$C_9H_{18}NO_2$[e]	C	C	1 499(5)	1 499(5)	1 291(7)	116 2(5)	116 2(5)	125 4(5)	23

[a] Mean and s d from mean (in parentheses) of six independent determinations [b] Mean and s d from mean (in parentheses) of three independent determinations
[c] L is the ligand N,N'-dimethyl N,N'-bis(β-mercaptoethyl)ethylenediamine [d] This is a nitroxyl free radical containing a five membered (C_4N) ring [e] This is a nitroxyl free radical containing a puckered six-membered (C_5N) ring

in Table 9 It is clear from Table 9 that there is much danger in attempting to compare structural data obtained for compounds of varying chemical composition and structure However, there is striking internal consistency in the results for the three free radicals Note that as the C—N—C angle increases from 114 8(5) to 123 9(5) to 125 4(5)° in XVII, XVIII, and XIX, respectively, the C—N and N—O distances also increase There is, at the same time, a decrease in the C—N—O angle which is very prominent between XVII and XVIII (or XIX). The lack of a difference in the C—N—O angle between XVIII and XIX is, no doubt, due to the small difference in their C—N—C angles However, the variations observed in these compounds are largely self-consistent and sensible

When we compare our results with those found for XIV, we note that the Co—N distance is identical with the Fe—N distance and that the two N—O distances also agree very well However, there are drastic differences in the values of the X—N—Y angles, the angle at the bridging nitrogen, and the metal—N—O and Y—N—O angles If we compare with XV, we note that the N—O distances disagree significantly (7 σ) even though one of the Y—N distances is nearly identical and the various angles listed are in closer agreement than between I and XIV Overall, the various angles at the nitrogen and the N—O distance in I resemble most those found in the nitroxyl series of free radicals Interestingly enough, the N—O stretching frequency in I is 1357 cm^{-1} which is quite close to that found in the nitroxyl series, viz. 1345 cm^{-1} [28]. This is a characteristic stretching frequency for these substances The stretching frequency normally associated with bridging NO groups is around 1550 cm^{-1}, as pointed out elsewhere by King [29]. The lowest frequency quoted for a bent nitrosyl group in the very complete and recent review on nitrosyl chemistry [30] is that for [Co-(das)$_2$(NO)(NCS)]$^+$ (das = o-phenylenebis(dimethylarsine)) where ν(NO) = 1587 and 1561 cm^{-1}. The metal—N—O angle in this compound is 134(2)°, quite close to that in I Thus, the 5,6-dinitrosonorbornene fragment of I behaves structurally and in its stretching frequency characteristics like a nitroxyl free radical

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