Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

The crystal and molecular structures of *N,N'*-ethylenebis(acetylacetoneiminato)- and *N,N'*-ethylenebis(benzoylacetoneiminato)nitrosylcobalt

R. WIEST and R. WEISS★
Laboratoire de Cristallochimie★★, Institut de Chimie, 1, rue B. Pascal, Strasbourg - 67 (France)
(Received March 18th, 1971)

The Schiff's base complexes of cobalt(II) *N,N'*-ethylenebis(acetylacetoneiminato)-cobalt(II) (Co(EA)) and *N,N'*-ethylenebis(benzoylacetoneiminato)cobalt(II) (Co(EB)) react with nitric oxide to give monomeric nitrosyl derivatives in which the chelate to nitric oxide molar ratio is 1/1[1]. The starting material is particularly interesting because its physico-chemical properties and reactivity show strong analogies with the vitamin B_{12} group compounds. Stable organometallic derivatives of Co(EA) with a cobalt–carbon bond are known[2] and a monomeric oxygen adduct $Co(O_2)L(EA)$, in which the cobalt oxygen linkage is probably bent, has been described[3].

In order to establish the geometry of the cobalt nitric oxide linkage in the nitrosyl derivatives of Co(EA) and Co(EB) we have determined their crystal structures. The existence of a bent M–N–O group has been suggested for $Co(NO)(S_2CNMe_2)_2$[4] and has been established in $[Ir(CO)Cl(NO)(PPh_3)_2]^{+}$[5] and $[Co(en)_2Cl(NO)]^{+}$[6] (en = ethylene-diamine).

Crystal data: crystals of Co(NO) (EA) and Co(NO) (EB) were prepared by the method of Tamaki *et al.*[1].

Co(NO) (EA) (orthorhombic), $a = 17.308(10)$, $b = 12.725(7)$, $c = 6.316(4)$ Å, $V = 1391$ Å^3, $D_{ob} = 1.45$, $D_c = 1.48$ g·cm^{-3}, $Z = 4$, Space group $P2_12_12_1$. Co(NO) (EB) (orthorhombic), $a = 22.188(10)$, $b = 11.935(5)$, $c = 7.708(2)$, $V = 2041$ Å^3, $D_{ob} = 1.39$, $D_c = 1.40$ g·cm^{-3}, $Z = 4$, Space group $P2_12_12_1$.

X-ray data were collected on a Picker four circle automatic diffractometer using MoKα radiation. The structures were solved by standard methods. R values are now 0.056 for 1232 reflections measured with Co(NO)(EA) and 0.070 for 1130 reflections obtained with Co(NO)(EB).

The molecular structure of Co(NO)(EA) is shown in Fig.1 with 30% probability ellipsoids drawn on the atomic sites. The Co(EA) group has the same geometry as in *N,N'*-ethylenebis(acetylacetoneiminato)methylcobalt(III) and apart from the presence of two phenyl rings instead of two methyl groups the geometry of the Co(EB) group in Co(NO)(EB) is not significantly different. The coordination arrangement around the cobalt atom is a

★Author to whom correspondence should be addressed.
★★Equipe de Recherche associée au C.N.R.S.

tetragonal pyramid with the nitrosyl group in the apical position. The oxygen and nitrogen atoms O(1), O(2), N(1) and N(2) are coplanar, the cobalt atom is displaced 0.19 Å in Co(NO)(EA) and 0.23 Å in Co(NO)(EB) out of this plane towards the nitrosyl group.

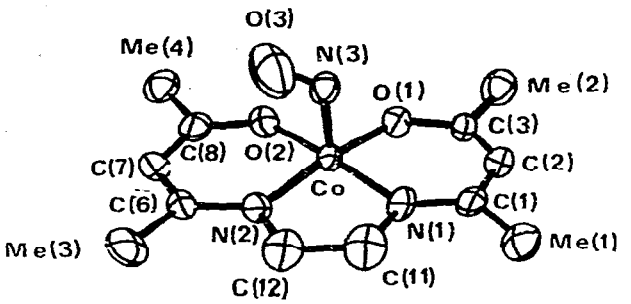

Fig.1. Molecular structure of Co(NO)(EA).

The Co–N–O linkage is distinctly bent in the two compounds; the angle is 122.4(0.5)° in Co(NO)(EA) and 122.9(0.8)° in Co(NO)(EB). The Co–N(NO) distances, of 1.82(1) and 1.83(1) Å respectively are significantly shorter than the average Co–N(EA) and Co–N(EB) distances of 1.89(1) and 1.88(1). A similar angle and similar distances have been found in the Co–N–O group of $[Co(Cl)(NO)(en)_2]^{+6}$.

Thus, the NO groups with an sp^2 hybridized nitrogen atom is probably bonded to a cobalt(III) atom with a concommittant π interaction occurring between Co and NO. Presumably, it is the same type of bond as that which occurs between the cobalt atom and the vinyl group in $Co(CH{=}CH_2)(H_2O)(EA)$[7].

REFERENCES

1 M. Tamaki, I. Masuda and R. Shinra, *Bull. Chem. Soc. Japan*, 42 (1969) 2858.
2 G. Costa, G. Mestroni, G. Tauzher and L. Stefani, *J. Organometal. Chem.*, 6 (1966) 181; G. Costa and G. Mestroni, *J. Organometal. Chem.*, 11 (1968) 325.
3 A.L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, 92 (1970) 55; B.M. Hoffmann, D.K. Diemente and F. Basolo, *J. Amer. Chem. Soc.*, 92 (1970) 61.
4 P.R.H. Alderman and P.G. Owston, *Nature*, 178 (1956) 1071; P.R.H. Alderman, P.G. Owston and J.M. Rowe, *J. Chem. Soc.*, (1962) 668;
5 D.J. Hodgson and J.A. Ibers, *Inorg. Chem.*, 7 (1968) 2345.
6 D.A. Snyders and D.L. Weaver, *Chem. Commun.*, 2 (1969) 1425.
7 S. Brückner, M. Calligaris, G. Nardin and L. Randaccio, *Inorg. Chim. Acta*, 3 (1969) 308; S. Brückner, M. Calligaris, G. Nardin and L. Randaccio, *Ibid.*, 2 (1968) 416.