X-ray structure analysis of the cobalt(III) complex formed with the ambidentate ligand 3-hydroxyiminopentane-2,4-dione: proof for N,O-*fac*-coordination and resonance charge delocalization

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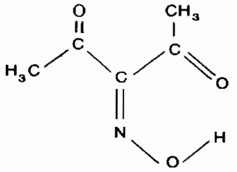
Abstract

The complex [Co(inaa)$_3$] (inaa = anion of 3-hydroxyiminopentane-2,4-dione) crystallizes in the triclinic space group $P\bar{1}$ with $a = 1549.8(8)$, $b = 1174.2(6)$, $c = 1127.1(5)$ pm, $\alpha = 111.95(2)$, $\beta = 94.73(2)$ $\gamma = 90.71(2)°$ and $Z = 4$. The three ambidentate ligands are attached to the Co through N and O atoms, forming five-membered chelate rings. The N_3O_3 set of donor atoms forms a distorted octahedron around the Co with the three N and O atoms being in a facial arrangement. The unit cell contains two pairs of enantiomers. The analysis of bond lengths points to strong resonance charge delocalization within the coordinated ligands.

Introduction

The introduction of substituents in 3-position of pentane-2,4-diones can lead to additional and/or competitive coordination modes of the ligands, depending on the nature and coordinating properties of the 3-substituents [1]. 3-Hydroxyiminopentane-2,4-dione, otherwise named isonitrosoacetylacetone and abbreviated to Hinaa therefore, represents such an ambidentate ligand, the coordination of which could, in principle, be of the O,O or O,N type. The orange–red, neutral cobalt(III) complex [Co(inaa)$_3$], first described by Taylor and Ewbank in 1926 [2], is diamagnetic and monomeric in solution. Patel and Halder [3] concluded from ^{1}H NMR and IR studies that, in this complex, the ligand is attached to the metal through N and O atoms, forming a five-membered chelate ring. The same conclusion was drawn by Butler *et al.* [4] from the NMR and IR data obtained for the intensively blue-colored iron(II) complex Na[Fe(inaa)$_3$]. On the basis of NMR evidence, they suggested the iron complex to be the facial isomer [4].



= Hinaa

The present study provides the results of the first X-ray single crystal structure analysis of the complex [Co(inaa)$_3$], which proves N,O-*fac*-coordination and, in addition, charge delocalization within the coordinated ligand.

Experimental

Preparation of [Co(inaa)$_3$]

Hinaa [5] and [Co(inaa)$_3$] [2, 6] were prepared as described and characterized by elemental analysis, UV–Vis and IR spectroscopy. The single crystal of [Co(inaa)$_3$] selected for X-ray structure analysis was obtained by recrystallization from chloroform/petroleum ether.

X-ray structure determination

The crystal chosen for analysis was the edge of a plate with the dimensions 0.12×0.25×0.65 mm. Intensities were measured with a four-circle diffractometer (Stoe-Stadi-4) using graphite-monochromatized Mo Kα radiation ($\lambda = 71.069$ pm). Cell constants were determined by least-squares methods from the 2θ angles of

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TABLE 1. Summary of crystal data for the complex [Co(inaa)$_3$]

Formula	$C_{15}H_{18}CoN_3O_9$
Molecular weight	443.26
Space group	triclinic, $P\bar{1}$
a (pm)	1549.8(8)
b (pm)	1174.2(6)
c (pm)	1127.1(5)
α (°)	111.95(2)
β (°)	94.73(2)
γ (°)	90.71(2)
Z	4
D_{calc} (g cm^{-1})	1.55
Reflections collected	7009
(2θ range up to 50)	–
Symmetry-independent reflections	4970
Reflections with $F > 2\sigma(F)$	4333
$R_1 = \Sigma \lvert F_o - F_c \rvert / \Sigma F_o$	0.0629
$R_2 = \Sigma w^{1/2} \lvert F_o - F_c \rvert / \Sigma w^{1/2} \lvert F_o \rvert$	0.0494
Absorption coefficient (cm^{-1})	9.5

TABLE 2. Final positional parameters (excluding hydrogens) for [Co(inaa)$_3$]

Atom	*x/a*	*y/b*	*z/c*
Co1	0.1858(1)	0.2513(1)	0.2858(1)
C1	0.1902(4)	−0.1141(5)	0.0612(6)
C2	0.1682(4)	0.0112(5)	0.1460(5)
O1	0.2276(2)	0.0916(3)	0.1962(4)
C3	0.0816(3)	0.0434(5)	0.1732(5)
N1	0.0774(3)	0.1652(4)	0.2398(4)
O2	0.0089(2)	0.2162(3)	0.2721(4)
C4	0.0045(4)	−0.0443(6)	0.1322(7)
O3	0.0078(3)	−0.1383(4)	0.0408(5)
C5	−0.0712(4)	−0.0162(7)	0.2070(8)
C6	0.4282(3)	0.3572(5)	0.4733(7)
C7	0.3358(3)	0.3119(5)	0.4324(6)
O4	0.3029(2)	0.3185(3)	0.3303(4)
C8	0.2840(4)	0.2623(5)	0.5031(6)
N2	0.2031(3)	0.2317(4)	0.4439(4)
O5	0.1449(2)	0.1887(3)	0.4868(4)
C9	0.3145(5)	0.2445(6)	0.6255(7)
O6	0.3914(3)	0.2439(6)	0.6501(6)
C10	0.2508(5)	0.2309(6)	0.7103(6)
C11	0.1156(4)	0.4062(6)	0.0235(6)
C12	0.1340(3)	0.3786(5)	0.1419(6)
O7	0.1732(2)	0.2808(3)	0.1290(3)
C13	0.1121(3)	0.4539(5)	0.2679(5)
N3	0.1406(3)	0.4081(4)	0.3567(5)
O8	0.1359(2)	0.4607(3)	0.4724(4)
C14	0.0613(4)	0.5682(5)	0.2981(7)
O9	0.0337(3)	0.5950(5)	0.2085(5)
C15	0.0432(3)	0.6426(5)	0.4300(6)
Co2	0.6909(1)	0.1766(1)	0.3156(1)
C16	0.6245(4)	−0.1369(6)	−0.0022(6)
C17	0.6305(4)	−0.0294(5)	0.1239(6)
O10	0.6946(2)	0.0449(3)	0.1516(4)
C18	0.5675(3)	−0.0102(5)	0.2135(6)
N4	0.5908(3)	0.0875(4)	0.3222(5)
O11	0.5500(2)	0.1200(4)	0.4181(4)
C19	0.4835(4)	−0.0828(6)	0.1925(8)
O12	0.4623(4)	−0.1544(7)	0.0878(7)
C20	0.4313(4)	−0.0687(7)	0.2961(7)
C21	0.8499(3)	0.4044(5)	0.2177(6)
C22	0.7746(4)	0.3341(5)	0.2392(6)
O13	0.7925(2)	0.2593(3)	0.2933(4)
C23	0.6863(3)	0.3468(5)	0.2040(5)
N5	0.6316(3)	0.2707(4)	0.2342(5)
O14	0.5538(2)	0.2656(4)	0.2154(4)
C24	0.6558(4)	0.4333(6)	0.1410(6)
O15	0.7087(3)	0.4875(5)	0.1093(6)
C25	0.5619(4)	0.4509(7)	0.1240(8)
C26	0.8242(4)	0.1016(5)	0.6057(6)
C27	0.7678(4)	0.1545(5)	0.5261(6)
O16	0.7608(2)	0.0946(3)	0.4051(4)
C28	0.7245(3)	0.2658(4)	0.5773(5)
N6	0.6856(3)	0.2946(4)	0.4804(4)
O17	0.6483(2)	0.3918(3)	0.5022(4)
C29	0.7182(4)	0.3346(5)	0.7142(6)
O18	0.7660(3)	0.3109(4)	0.7921(4)
C30	0.6520(4)	0.4260(6)	0.7577(6)

84 reflections ($T = 25$ °C), measured on the same instrument.

The measured intensities were corrected for background and Lp effects; a numerical absorption correction was applied.

The structures were solved by direct methods and atomic positions and anisotropic temperature factors refined by least-squares methods to the R values given in Table 1. Final parameter shifts were less than 0.1 standard deviations. Hydrogen atoms were positioned geometrically (C–H distance 108 pm) and not refined. The crystallographic calculations were performed with the programs SHELX-76 and SHELXS-86 on an IBM 200 D computer at Technische Hochschule Darmstadt, using scattering factors for C, H, N and O as stored in SHELX-76. The scattering factor for Co was taken from ref. 7. Table 1 summarizes relevant crystallographic data and information on data processing. The final positional parameters are given in Table 2; the bond distances and bond angles in Table 3.

Results and discussion

As summarized in Table 1, [Co(inaa)$_3$] crystallizes in the triclinic space group $P\bar{1}$, with 4 molecules in the unit cell. The structure could be refined to $R_2 = 0.0494$. The coordination of the two symmetry-independent molecules A (with Co(1)) and B (with Co(2)) is very similar; distances and bond angles of the three identical ligands are in the same range for both molecules. Figure 1 gives a view of the coordination geometry of molecule A which shows that (i) the anionic ligand inaa$^-$ is N,O-coordinated in a bidentate fashion, forming a five-membered chelate ring, (ii) the overall N_3O_3 coordination is of octahedral geometry, and (iii) the complex has a facial arrangement of the O and N atoms, respectively. The bidentate N,O-coordination of the ligands in [Co(inaa)$_3$] is thus in line with the results

TABLE 3. Selected interatomic distances (pm) and bond angles (°) in [Co(inaa)$_3$]

Distances[a]			
Co(1)–N(1)	188.0(4)	C(1)–C(2)	149.1[b]
Co(1)–N(2)	187.9(5)	C(2)–C(3)	143.2[b]
Co(1)–N(3)	188.3(4)	C(3)–C(4)	150.2[b]
Co(1)–O(1)	191.7(3)	C(4)–C(5)	147.1[b]
Co(1)–O(4)	191.9(3)	C(2)–O(1)	125.6[b]
Co(1)–O(7)	191.8(4)	C(4)–O(3)	120.6[b]
		C(3)–N(1)	134.9[b]
		N(1)–O(2)	123.6[b]
Angles[a]			
N(1)–Co(1)–O(1)	83.0(2)	N(3)–Co(1)–O(4)	91.9(2)
N(2)–Co(1)–O(4)	83.0(2)	O(1)–Co(1)–O(4)	90.0(2)
N(3)–Co(1)–O(7)	83.7(2)	O(1)–Co91)–O(7)	90.4(2)
N(1)–Co(1)–N(2)	94.1(2)	O(4)–Co(1)–O(7)	93.8(2)
N(1)–Co(1)–N(3)	95.4(2)	N(1)–Co(1)–O(4)	172.3(2)
N(2)–Co(1)–N(3)	94.3(2)	N(2)–Co(1)–O(7)	176.2(2)
N(1)–Co(1)–O(7)	89.3(2)	N(3)–Co(1)–O(1)	174.0(2)
N(2)–Co(1)–O(1)	91.6(2)		

[a] The distances and angles for the molecule A with Co(1) are close to those of the molecule B with Co(2). [b] The data listed are averaged data for the three ligands present in [Co(1)(inaa)$_3$].

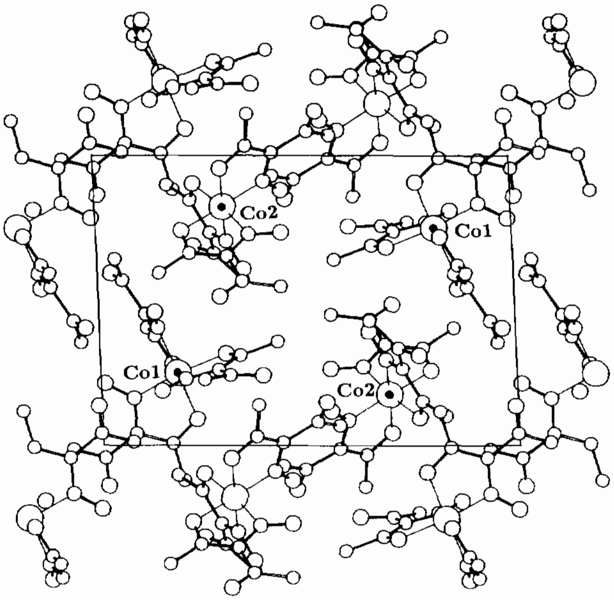


Fig. 2. View of the unit cell of [Co(inaa)$_3$] showing the two pairs of enantiomers (projection along the c axis).

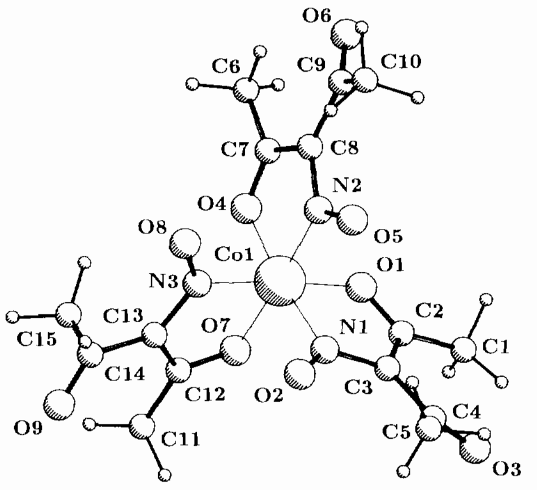
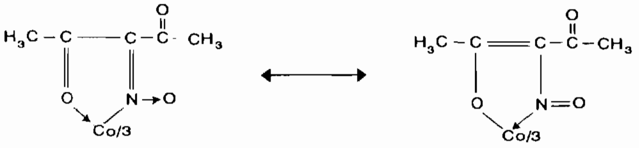


Fig. 1. View of the coordination geometry in the left-handed enantiomer [Co(1)(inaa)$_3$].

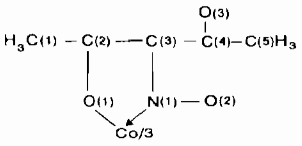
of the X-ray structure analysis of the complex *cis*-[Co(inaa)$_2$(py)$_2$]ClO$_4$, as carried out by Tamura *et al.* [8].

It follows from the angles listed in Table 3 that the octahedral coordination is distorted. The O–Co–N angle within each of the three coordinated ligands is 83° only and all of the N–Co–N, O–Co–O and N–Co–O angles deviate slightly from 90 and 180°, respectively. The packing of the molecules in the unit cell is such that one enantiomer is sitting on top of the other (see Fig. 2). There is obviously no bonding interaction between them and no chain formation.

On the basis of NMR and IR data, Patel and Haldar [3] discussed structures **I** and **II** to be canonical forms of [Co(inaa)$_3$]. The bond distances within the coordinated ligand inaa$^-$ (see Table 3 and **III**) contribute significantly to this discussion. None of the C–C distances found corresponds to either the normal C–C bond (154 pm) or the normal C=C double bond (134 pm). There are relatively short distances (such as C(2)–C(3) = 143.2 pm) and relatively long ones (such as C(3)–C(4) = 150.2 pm), whereas some are in between. The C(2)–O(1) distance of the coordinated keto (or enol) group is considerably longer (125.6 pm) than the C(4)–O(3) distance of the free acetyl group (120.6 pm), which is close to normal (119 pm). Compared to the normal C–N bond (147 pm) and C=N double bond (122 pm), the observed C(3)–N(1) distance of 134.9 pm again lies in between and the same is true for the N(1)–O(2) bond of the oxime group (123.6 pm). In summary, the detailed discussion of bond lengths and bond orders leads to the conclusion that structure **IV**

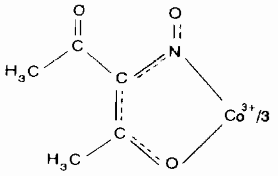


I **II**



III

appears to be a reasonably adequate description of the bonding situation in [Co(inaa)$_3$] as well as in *cis*-[Co(inaa)$_2$(py)$_2$]ClO$_4$ [8]. This means that there is indeed strong resonance charge delocalization within the coordinated ligand.



IV

Supplementary material

Further information concerning details of the structure analysis is available from the authors on request.

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References

1 O. Angelova, J. Maciceck, M. Atanasov and G. Petrov, *Inorg. Chem., 30* (1991) 1943.
2 T. W. J. Taylor and E. K. Ewbank, *J. Chem. Soc.,* (1926) 2818.
3 N. J. Patel and B. C. Haldar, *J. Inorg. Nucl. Chem., 29* (1967) 1037.
4 A. R. Butler, A. M. Calsy and C. Glidewell, *Polyhedron, 8* (1989) 175.
5 L. Wolff, P. Bock, G. Lorentz and P. Trappe, *Liebigs Ann. Chem., 325* (1902) 139.
6 W. Küster, *Z. Physiol. Chem., 154* (1926) 157.
7 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974.
8 H. Tamura, K. Ogawa, R. Ryu, M. Tanaka, T. Shono and I. Masuda, *Inorg. Chim. Acta, 50* (1981) 101.