

Structure determination of two metal-organic complexes from high-resolution synchrotron powder diffraction data

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The crystal structures of [1,2-bis(2,6-diisopropylphenylimino)acenaphthene-*N,N'*]carbonylchlororhodium(I) (**1**) and [*N,N'*-ethylenebis(3-methylsalicylideneiminato)-*O,N,N',O'*](tetrahydrofurfuryl)cobalt(II) (**2**) have been determined from high-resolution synchrotron X-ray powder diffraction data. Compound **1** is the first neutral Rh complex, in contrast with findings in the literature, containing a bidentate nitrogen ligand, and compound **2** is the first three-dimensional structure of a (five-coordinated) tetrahydrofurfurylcobalt(III) complex. Grid-search and Rietveld refinement have been used to determine and refine the structures, respectively. Crystals of **1** are orthorhombic, space group *Pbca*, *Z* = 8, with cell parameters *a* = 21.729 (2), *b* = 27.376 (3), *c* = 11.580 (1) Å. Crystals of **2** are monoclinic, space group *P2₁/n*, *Z* = 4, *a* = 16.6701 (6), *b* = 9.4170 (4), *c* = 13.7088 (7) Å and β = 96.520 (3)°. Chemical diagrams for the two compounds are given. Soft restraints were applied during Rietveld refinement; for **1** converging to R_p = 8.4%, R_w = 11.0%, GoF = 2.3, and for **2** converging to R_p = 8.5%, R_w = 11.4%, GoF = 7.6.

Keywords: structure determination; powder diffraction; grid-search techniques.

1. Introduction.

The structure determinations presented in this paper are part of a series of attempts to determine crystal structures from X-ray powder diffraction data (Helmholdt *et al.*, 1998; Goubitz *et al.*, 1999, 2001; van Langevelde *et al.*, 1999; Dova *et al.*, 2001). The determination of crystal structures from single-crystal data has become a standard routine during the last decades provided it is possible to grow suitable crystals. If only powder is available then structure determination is certainly by no means a standard procedure. In the last decade a number of research groups have attempted to tackle this problem and a couple of program packages exist nowadays [*e.g.* *POWSIM* (Jansen *et al.*, 1992*a,b*, 1993), *SIRPOW* (Altomare *et al.*, 1994, 1995)]. The main problem in structure determination is the number of reflections with reliable intensity that can be extracted from a powder diffractogram. Particularly for lower symmetries (up to orthorhombic) and larger structures, the overlap of reflections often prevents the extraction of reliable intensities, especially at higher θ values. Standard *ab initio* determination procedures are hampered because data sets obtained from powder data are far from complete. The grid-search technique (Chernyshev & Schenk, 1998) used here can over-

come this problem for molecules with known conformation. Only the lower angle part of the diffractogram, where overlap of reflections is less severe, is needed to obtain a reliable estimate of the position and the orientation of the molecule within the asymmetric unit. Variation of proper torsion angles can result in a more reliable structural model that can be used as a starting point in a refinement procedure.

2. Chemical background.

Compound **1** is a Rh complex containing a bidentate nitrogen ligand. These complexes are of great interest because of their catalytic activity in several types of reaction such as hydroformylation (Saus *et al.*, 1983; Garcia *et al.*, 1985; Clauti *et al.*, 1986; Bayón *et al.*, 1991; Botteghi & Paganelli, 1993), hydrogenation (Mestroni *et al.*, 1977; Pasternak *et al.*, 1976; Pasternak & Pruchnik, 1976; Zassinovich *et al.*, 1976, 1977, 1987) and hydrogen transfer (Gillard *et al.*, 1975). These complexes are also known for their electrocatalytic capability in the reduction of carbon dioxide (Bollinger *et al.*, 1988). Compound **1** was prepared by reacting $[\text{Rh}(\text{CO})_2(\text{Cl})]_2$ with 2,6-diisopropylbis(phenylimino)acenaphthene in dichloromethane. Details of the synthesis will be published elsewhere (Mahabiersing *et al.*, 2001).

Organocobalt(III)salen complexes like **2** can be used as model compounds for coenzyme B₁₂ (5'-deoxyadenosylcobalamin). Similar to the coenzyme, the Co—C bond of (alkyl)Co(salen) complexes can be cleaved homolytically by heat or light to create a cobalt(II) complex and an alkyl radical. Co—C bond homolysis is the first step in a number of B₁₂-dependent enzymatic 1,2-rearrangement reactions (Halpern, 1985). The thus generated 5'-deoxyadenosyl radical abstracts an H atom from the substrate, after which a 1,2-migration occurs.

Structural investigations of the coenzyme and models thereof have provided valuable information on the relative weakness of the organometallic bond at the coenzyme (Toscano & Marzilli, 1984). A notable feature in the crystal structure of the coenzyme is the large Co—C—C angle of 125°. Since the tetrahydrofurfuryl ligand structurally resembles the 5'-deoxyadenosyl group, comparison of structural information on tetrahydrofurfurylcobalt(III) complexes with that of the coenzyme may show interesting similarities or differences. Tetrahydrofurfurylbromide was prepared according to a published procedure (Smith, 1955). (Tetrahydrofurfuryl)Co(3-mesalen) was synthesized by using the procedure for (*n*-butyl)Co(salen) (van Arkel *et al.*, 1993).

3. Experimental

X-ray powder diffraction photographs of these samples were taken using an Enraf–Nonius FR 552 Guinier Johansson camera (Enraf–Nonius, Delft, The Netherlands) equipped with a Johansson monochromator (Roberts & Parrish, 1962) using Cu $K\alpha_1$ radiation, λ = 1.54060 Å. The samples were prepared by pressing the powder into a thin layer onto Mylar foil. To improve particle statistics the sample holder was rotated in the specimen plane. For indexing of the patterns the accurate positions of as many lines as possible were collected by reading out the Guinier photographs with an optical instrument. Using a Johansson LS-18 microdensitometer the Guinier photographs were digitized from 4.0 to 84.2° 2θ in steps of 0.01° 2θ . Cell parameters and (possible) space groups were determined using the program *ITO* (Visser, 1969).

X-ray powder diffraction patterns of both compounds were measured at the high-resolution powder diffraction station BM16 (Fitch, 1996) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) with λ = 0.65296 Å for **1** and λ = 0.65052 Å for **2**.

The wavelength was calibrated by measuring 11 peaks from NIST Si standard 640b (lattice parameter certified as 5.43094 Å). These peaks were fitted with a pseudo-Voigt profile function to obtain peak positions, accounting for asymmetry using the Finger–Cox–Jephcoat correction, and then fitting the wavelength and instrumental zero point to these positions *via* least squares. For data collection a capillary with a diameter of 1.5 mm was filled with powder and rotated during exposure. Continuous scans were made from 0.0 to 25.0° 2θ for **1** and 0.0 to 30.0° 2θ for **2** with 0.5° $2\theta \text{ min}^{-1}$ and a sampling time of 50 ms. After data collection the scans were binned at 0.005° 2θ .

All data collections were performed at room temperature.

4. Structure solution and refinement

To obtain reflection intensities a full-pattern decomposition (FPD) procedure using the program *MRIA* (Zlokazov & Chernyshev, 1992) was performed: the high-resolution synchrotron powder diffraction patterns were fitted employing a split-type pseudo-Voigt peak profile function (Toraya, 1986). Some details of the FPD procedure are listed in Table 2.

Initial models of both compounds were built from similar complexes searched for in the Cambridge Structural Database (CSD) (Allen & Kennard, 1993) and the necessary changes were made using the program package *Cerius²* (Molecular Simulations Inc., 1995). Compound **1** (Fig. 1) could be built from the CSD entry WETGIL (van Asselt *et al.*, 1994); replacing Pd by Rh and the CH₃ group by CO yielded the desired model, which was used in the grid-search procedure. For **2** the CSD entry ESALCP (Haller & Enemark, 1978) was used and by using *Cerius²* the molecule was completed with the tetrahydrofurfuryl moiety. This model was optimized using some cycles of energy minimization.

To position the molecule in the asymmetric part of the unit cell, the initial models were used in the grid-search procedure (Chernyshev & Schenk, 1998) performed by the program *MRIA*, using 50 low-angle X_{obs} [X_{obs} and $R(X)$ are defined in expressions (1) and (2) of Chernyshev & Schenk (1998)] values extracted from the patterns after the FPD procedure. The model was translated and rotated through the asymmetric unit. The initial grid increments were 0.6 Å for molecule

translations along a , b and c , and 30° for the three rotations around φ , ψ and κ angles. The minima found in this way were examined in more detail by gradually lowering the incremental steps in translation to 0.1 Å and in rotation to 0.5°, resulting in $R(X)$ values of 37.2 and 45.6%, respectively. For **2** the model was further refined by using a script that automatically varied two torsion angles τ_1 and τ_2 (Fig. 2) in steps of 5° each and that updated the input for the grid search. This resulted in a minimum $R(X)$ value of 35.1%.

The bond-restrained Rietveld refinement (RR) was performed using the same program suite *MRIA*. For both patterns the split-type pseudo-Voigt peak profile function (Toraya, 1986) was used. The preferred orientation was refined using the symmetrized harmonics expansion method (Ahtee *et al.*, 1989; Järvinen, 1993).

In order to retain chemically realistic models a bond-restrained RR as described by Baerlocher (1993) was applied to all interatomic distances up to 3.0 Å (with $\sigma = 1\%$ of the ideal distance). The weight c_w (Baerlocher, 1993, p. 188) that weighs the residual function of the restraints S_R versus the Rietveld residual S_Y was gradually reduced from 209.4 to 1.0 for **1** and from 46.5 to 0.2 for **2**.

During the refinement the U_{iso} values of identical atom types were coupled. The relevant crystal data and the results of the refinements are presented in Tables 1 and 2, respectively; selected bond distances and angles are listed in Tables 3 and 4.† Plots of the observed and calculated X-ray diffraction patterns and difference plots after RR and *PLUTON* (Spek, 1990) plots of both compounds are depicted in Figs. 3–6.

5. Discussion

5.1. Structural features of **1**

After the RR, inspection of the observed and calculated pattern revealed some residual intensity. The shoulder at 4.3° and the single peak at 4.7° and other peaks in the difference pattern are considerably broader than the peaks belonging to Bragg reflections, suggesting some impurity in the sample. This could also explain the rather high peak in the difference pattern at 3.4°, because that peak has the same shape as the peaks mentioned before (Fig. 7). The same

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: WL2002). Services for accessing these data are described at the back of the journal.

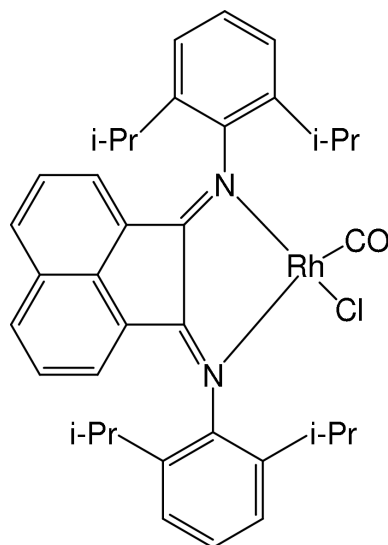


Figure 1
Chemical diagram of **1**.

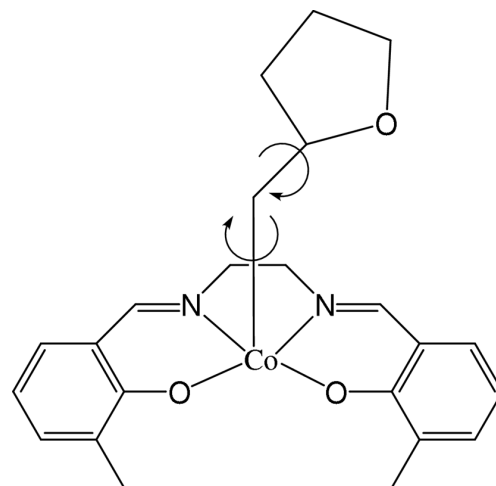


Figure 2
Chemical diagram of **2** (the torsion angles varied are indicated by arrows).

Table 1
Crystallographic data for compounds **1** and **2**.

	1	2
Formula	C ₃₇ H ₄₀ N ₂ OCIRh	C ₂₃ H ₂₇ N ₂ O ₃ Co
Space Group	<i>Pbca</i>	<i>P2₁/n</i>
<i>a</i> (Å)	21.729 (2)	16.6701 (6)
<i>b</i> (Å)	27.376 (3)	9.4170 (4)
<i>c</i> (Å)	11.579 (1)	13.7088 (7)
β (°)		96.520 (3)
<i>V</i> (Å ³)	6888 (2)	2138.1 (2)
<i>Z</i>	8	4
Wavelength (Å)	0.65296	0.65051
<i>D_x</i> (g cm ⁻³)	1.29	1.35
<i>F</i> (000) (electrons)	2768	920

Table 2
Details of the bond-restrained Rietveld refinement.

$R_p = \sum |y_{\text{obs}} - y_{\text{calc}}| / \sum y_{\text{obs}}$, $R_{wp} = \sum w(y_{\text{obs}} - y_{\text{calc}}) / \sum w y_{\text{obs}}$. The second line for GoF, R_p and R_{wp} indicates the results of the FPD procedure.

	1	2
<i>M</i> ₂₀	25.1	14.0
2 θ region (°)	2.5–25.0	0.01–30.00
Number of datapoints	4500	5999
Number of reflections	1102	1182
Number of restraints	377	276
Number of variables		
Structural		
Lattice	3	4
Positional	126	87
Thermal	5	4
Other		
Texture	9	15
Profile	19	19
Background	12	12
Zero shift	1	1
GoF	2.5	7.6
	2.3	8.0
<i>R_p</i> (%)	8.4	8.5
	7.7	8.6
<i>R_{wp}</i> (%)	11.1	11.4
	10.3	11.8

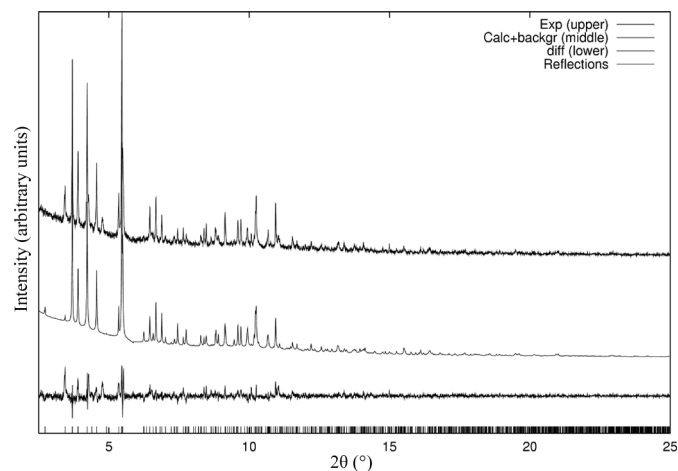


Figure 3
Bond-restrained RR of **1**. The upper curve illustrates the observed data, the middle curve illustrates the calculated data, while the lower curve shows the difference between the observed and calculated data. Markers of all reflections are included at the bottom.

Table 3
Selected distances (Å) and angles (°) for **1**.

Rh—Cl	2.25 (3)	Rh—N2	2.06 (3)
Rh—N1	2.06 (3)	Rh—C13	1.99 (4)
Cl—Rh—N1	174.0 (10)	N1—Rh1—N2	80.0 (10)
Cl—Rh—N2	94.3 (9)	N1—Rh1—C13	94.3 (11)
Cl—Rh—C13	91.5 (10)	N2—Rh1—C13	174.2 (12)

Table 4
Selected distances (Å) and angles (°) for **2**.

Co—O1	1.84 (4)	Co—N2	1.94 (6)
Co—O2	1.94 (5)	Co—C19	2.04 (6)
Co—N1	1.86 (7)		
O1—Co—O2	88 (2)	O2—Co—N2	92 (3)
O1—Co—N1	96 (2)	O2—Co—C19	84 (3)
O1—Co—N2	178 (2)	N1—Co—N2	84 (3)
O1—Co—C19	90 (2)	N1—Co—C19	94 (3)
O2—Co—N1	175 (2)	N2—Co—C19	93 (2)

applies to some other peaks in the low-angle region of the difference pattern. During the Guinier measurements these same peaks were present in the first photograph, but photographs taken from the same sample a couple of hours later no longer showed these peaks. This suggests the presence of a solvent that, under the vacuum conditions in the Guinier–Johansson camera, (slowly) evaporated. The capillary used for measuring the synchrotron data was filled and closed immediately, so evaporation of possible solvent could be prevented.

The bond distances and angles are similar to those found in comparable complexes in the literature. All aromatic rings are planar and the coordination of the Rh atom is a regular octahedron.

Meanwhile, from **1**, a single-crystal structure has also been determined (Mahabiersing *et al.*, 2001). In that structure a solvent molecule (acetone) is present and the crystals are tetragonal with space group *I4₁/a*. Matching identical atoms of both structures led to an r.m.s. of 0.44 Å, the largest differences occurring in the diisopropylphenyl moieties (not taking those into account in the match led to an

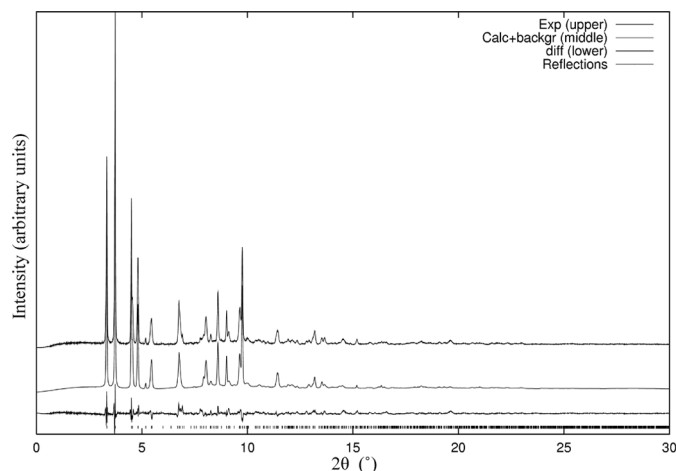


Figure 4
Bond-restrained RR of **2**. The upper curve illustrates the observed data, the middle curve illustrates the calculated data, while the lower curve shows the difference between the observed and calculated data. Markers of all reflections are included at the bottom.

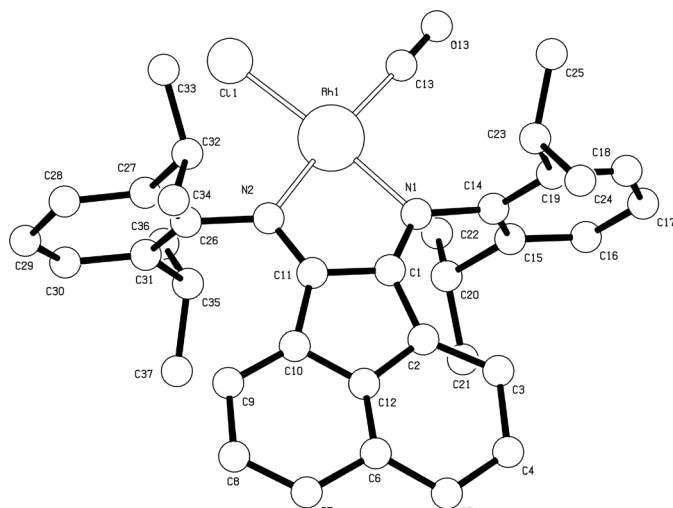


Figure 5
PLUTON plot of **1** after bond-restrained RR.

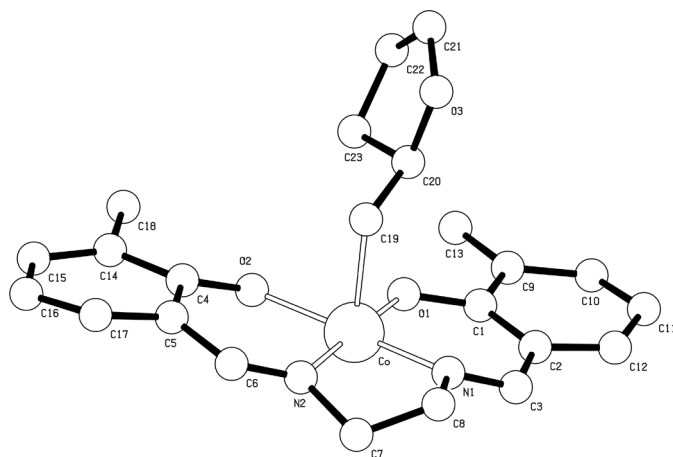


Figure 6
PLUTON plot of **2** after bond-restrained RR.

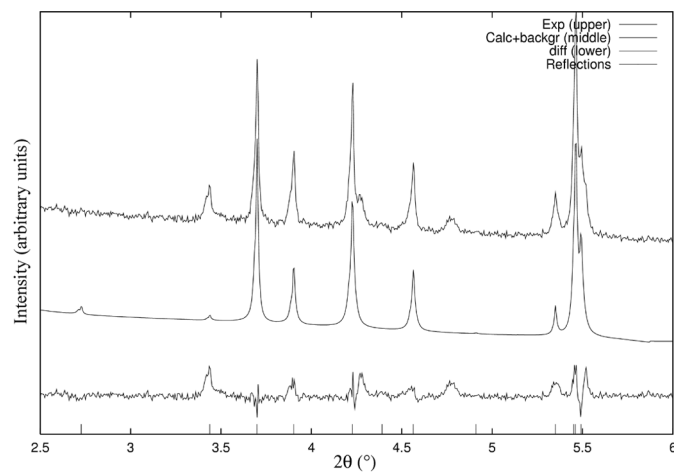


Figure 7
Lower-angle part of the diffraction pattern of **1** (see §5.1)

r.m.s. value of 0.10 Å). This is further evidence that the methods described in this paper lead to correctly determined and refined structures.

5.2. Structural features of **2**

Compound **2** could only be refined by employing a very small damping factor (0.005) to avoid destroying the geometry of the molecule during refinement. Examination of the sample and the powder pattern revealed that this powder was of poor quality (maybe due to the crystallinity and/or particle size) and hardly any significant diffraction signal was present at diffraction angles beyond $20^\circ 2\theta$; this may have caused the difficulties encountered during refinement. It is also noticeable that the full width at half-maximum of **1** is considerably smaller (minimum 0.014) than that of **2** (minimum 0.038). Attempting to refine **2** without the heavy damping was not successful; the only atoms that could be refined were the Co atom and the five atoms directly bonded to it, and every attempt to decrease the bond restraints or to release the other atomic positions failed; this RR converged to $R_p = 10.3\%$.

Compound **2** is comparable with other Co-(salen) complexes from the literature. The equatorial atoms which are directly connected to the Co atom show some tetrahedral distortion which, in combination with the N,N' -ethylene bridge, lead to a slight deviation from planarity of both aromatic rings. This tetrahedral distortion was also observed in cobaloximes by De Ridder *et al.* (1996, and references therein). The tetrahydrofurfuryl moiety is almost perpendicular to the rest of the molecule.

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