of $Co(OH_2)_6^{2+}$ ions (along *c*) would be an ordered array of alternating vacant and occupied Co sites. However, with 41.4% occupancy, the sites are randomly occupied in all three dimensions.

The cobalt bis(oxalato)platinate salt, as described to this point, is essentially isostructural with the magnesium salt, $Mg_{0.82}[Pt(C_2O_4)_2]\cdot 5.3H_2O$, as reported by Krogmann.[5] However, we have located a "new" water site which is not within the Co^{2+} coordination sphere but appears to be disordered about the special position ($^1/_4$, $^3/_4$, 0) as indicated by its elongated thermal ellipsoid (see Table II). This new water molecule appears to be strongly hydrogen bonded to one of the coordinated water molecules, with O(8)···O(5) = 2.695 (9) Å. Apparently it is not bonded to any of the oxalate ligand atoms. Therefore, on the basis of x-ray analysis, each cobalt bis(oxalato)platinate unit is hexahydrated. This result has been confirmed by thermal gravimetric analysis[17] of $Co_{0.83}[Pt(C_2O_4)_2]\cdot 6H_2O$. Since in all other respects the Co and Mg salts are isostructural, one may reasonably speculate that the Mg salt also contains this additional water molecule.

The introduction of the d^7 Co^{2+} ion into the lattice of a partially oxidized one-dimensional conductor is the first example of a paramagnetic transition-metal counterion in this role. Studies of the magnetic and electrical conduction properties of $Co_{0.83}[Pt(C_2O_4)_2]\cdot 6H_2O$ are in progress.

Acknowledgment. Research at Argonne National Laboratory is performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy. J.M.W. and A.E.U. gratefully acknowledge the support of NATO under grant No. 1276. A.E.U. also thanks Johnson Matthey & Co. for the loan of platinum salts.

Registry No. $Co[Pt(C_2O_4)_2]\cdot 6H_2O$, 65681-92-7; $AgPt(C_2O_4)_2$, 65681-91-6.

Supplementary Material Available: A listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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(11) All least-squares refinements were based on minimization of $\sum_i w_i|F_o^2 - S^2F_c^2|$, where *S* is the scale factor and the individual weights $w_i = 1/\sigma^2(F_o^2)$. Scattering factors are from ref 9b with Pt and Co treated for anomalous scattering.
(12) $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$, $R(F_o^2) = \sum|F_o^2 - F_c^2|/\sum F_o^2$, and $R_w(F_o^2) = [\sum w_i|F_o^2 - F_c^2|^2/\sum w_iF_o^4]^{1/2}$.
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Crystal and Molecular Structure of a One-Dimensionally Stacked Binuclear Rhodium(I) Complex Containing a Tetradentate Dibenzoylhydrazido Ligand

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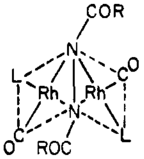
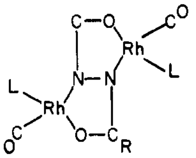
Received October 10, 1977

The binuclear rhodium(I) complex $[(CO)_2RhNCOC_6H_5]_2$ has been shown by a crystal structure analysis to contain a dibenzoylhydrazido group with a novel tetradentate bridging configuration. Crystals of μ-*N*,*N'*-dibenzoylhydrazido-(*N*,*N'*,*O*,*O'*)-bis(dicarbonylrhodium) are monoclinic, space group *I*2/*a*, with four molecules in a cell of dimensions *a* = 10.421 (14) Å, *b* = 14.795 (23) Å, *c* = 11.667 (17) Å, and β = 94.63 (3)°. The structure determination was based upon 727 diffraction maxima with 2θ(Mo Kα) ≤ 45°. Full-matrix anisotropic least-squares refinement converged to a final conventional discrepancy factor of 0.046. The crystal structure is made up of centrosymmetric dimers, with the dibenzoylhydrazido ligand utilizing all four of its nitrogen and oxygen atoms to form five-membered chelate rings at each square-planar Rh atom. Bond distances within the chelate ring include Rh–N = 2.071 (10) Å, N–N = 1.398 (18) Å, N–C = 1.309 (16) Å, C–O = 1.255 (15) Å, and O–Rh = 2.028 (9) Å. This structure is believed to be a prototype for a series of related Rh(I) and Ir(I) complexes. The molecules exhibit one-dimensional stacking in the crystal, with Rh–Rh contacts of 3.347 (5) Å between adjacent dimers.

Introduction

The reaction of *mer*-$RhCl_3L_3$ (L = PMe_2Ph, PPh_3) with 1,2-dibenzoylhydrazine was reported in 1972 by Hussein and Kasenally to yield a dimeric product, $[L(CO)RhN(COPh)]_2$, for which the N-bridged structure I was suggested.[1] This proposed structure was closely related to that of $[Rh(CO)_2Cl]_2$[2] and contained a substituted hydrazo bridging ligand similar to those which have been found in a series of dimeric bis(tricarbonyliron) species.[3-5] An alternative structure II for the rhodium dimer was proposed by Ittel and Ibers, who found the N,O-chelating configuration III for the dibenzoylhydrazido ligand in $Pt(PPh_3)_2(PhCONNCOPh)$.[6] A number of analogues of the rhodium dimer were subsequently reported by Kasenally and Hussein.[7] These workers found no definitive basis for distinction between structures I and II, though they tended to favor II.


I (L = C_6H_5)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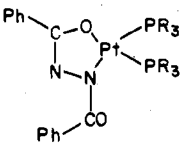
III

A potentially interesting aspect of the proposed structures is the electronic nature of the bridging ligand, which could be

Table I. Crystal Data and Experimental Parameters

A. Crystal Data

Formula	$Rh_2C_{18}H_{10}N_2$	V, Å^3	1793.1 (45)
Formula wt	556.10	Z	4
a, Å	10.421 (14)	Density (obsd), g cm^{-3}	2.0 (1)
b, Å	14.795 (23)	Density (calcd), g cm^{-3}	2.06
c, Å	11.667 (17)	Space group	$I2/a$
β, deg	94.63 (3)°	μ(Mo Kα)	18.3 cm^{-1}

B. Experimental Parameters

Radiation	Mo Kα λ(Kα_1) 0.70930 Å, 0.003 in Nb filter	Scan rate	1°/min in 2θ
		Scan range	−0.60° from Kα_1 to +0.50° from Kα_2
Temp, °C	22	Background counting	20-s fixed counts each end of scan
Receiving aperture	5 mm square, 30 cm from crystal	2θ(max), deg	45
Takeoff angle, deg	2.0	Data collected	1262
		Data with $F_o^2 > 3\sigma(F_o^2)$	727

present either as a substituted diazene or as a hydrazido group, or in some intermediate delocalized form. An additional point of interest is the possibility of metal–metal interactions of the sort found in $[Rh(CO)_2Cl]_2$[2] and in various complexes of square-planar d^8 metal ions.

In this paper are reported the results of a crystal structure analysis of $[(CO)_2RhN(COPh)]_2$, obtained from $[(PPh_3)(CO)RhN(COPh)]_2$ by high-pressure carbonylation.[7]

Experimental Section

Data Collection and Reduction. A sample of $[Rh(CO)_2(NCOC_6H_2)]_2$ was provided by Dr. A. S. Kasenally. Recrystallization from hot benzene yielded orange crystals, most of which were present as clusters of very small needles. A few somewhat larger needles, of cross section 0.05–0.07 mm, were also obtained. Preliminary precession photographs of several of these crystals displayed monoclinic symmetry, with systematic absences (hkl, $h + k + l \neq 2n$; $h0l$, $h \neq 2n$, $l \neq 2n$) consistent with space groups Ia and $I2/a$. Cell parameters were obtained by least-squares refinement of the setting angles of 12 reflections which had been accurately centered on a Picker four-circle x-ray diffractometer.[8] Owing to the small size of the crystals, the density could only be determined approximately by flotation in aqueous zinc bromide solution. Crystal data are summarized in part A of Table I.

The crystal used for collection of intensity data was of dimensions 0.05 × 0.05 × 0.15 mm, mounted with the needle axis (the a direction) approximately parallel to the diffractometer ϕ axis. Narrow-source open-counter ω scans through several reflections indicated a very low mosaic spread, as measured by an average full width at half-maximum of 0.07°. Data were collected by use of procedures previously described.[9] Experimental parameters are tabulated in part B of Table I. No reflections were strong enough to require attenuation. Four standard reflections were monitored after every 100 data; the intensities of these standards showed only random variations of magnitudes comparable to those expected on the basis of counting statistics. The data were processed by use of previously described methods.[9] A p factor of 0.05 was used in estimating the standard deviations of the observed intensities.

Structure Solution and Refinement. The coordinates of the rhodium atom were readily determined from a three-dimensional Patterson function, interpreted on the assumption of the centrosymmetric space group $I2/a$.[10] This assumption was verified by the subsequent successful solution of the structure. This space group, with $Z = 4$, requires the dimeric molecules to possess crystallographic 2 or $\bar{1}$ symmetry. A difference Fourier map, phased on the rhodium atom, yielded the coordinates of all remaining nonhydrogen atoms. Two cycles of isotropic refinement yielded discrepancy factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.064$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.070$. A single cycle of anisotropic refinement gave $R_1 = 0.050$ and $R_2 = 0.054$. A difference Fourier map calculated at this point clearly showed the five phenyl hydrogen atoms as peaks ranging from 0.56 to 0.93 e/Å^3 in height. The largest feature of this map not interpretable as a hydrogen atom was a peak of height 0.70 e/Å^3. Final refinement included fixed hydrogen atoms at their calculated positions (C–H = 0.95 Å, C–C–H = 120°) with assumed isotropic temperature factors of 4.5 Å^2. Anisotropic thermal parameters were employed for all other atoms. This refinement converged to $R_1 = 0.046$ and $R_2 = 0.051$. In the final cycle of refinement, no parameter shifted by more than one-fourth of its standard deviation.

In all structure factor calculations, atomic scattering factors (including anomalous terms for Rh) were taken from ref 11. The quantity minimized in least-squares refinements was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. The final standard deviation of an observation of unit weight was 1.24. Calculation of structure factors for the 535 data with $F_o^2 \leq 3\sigma(F_o^2)$ revealed four reflections with $\Delta(F^2) \geq 3\sigma(F_o^2)$; of these, none had $\Delta(F^2)/\sigma > 4$.

Final atomic positional and thermal parameters are listed in Table II. Intramolecular distances and angles are tabulated in Table III and selected intermolecular contacts are given in Table IV. Data on least-squares molecular planes are presented in Table V. Tables of observed and calculated structure factors and of principal amplitudes of thermal motion are available.[12]

Description of the Structure and Discussion

A view of the molecular structure of $[(CO)_2RhNCOPh]_2$ is shown in Figure 1. The two halves of the dinuclear molecule

Table II. Atomic Positional and Thermal Parameters for $[C_6H_5CONRh(CO)_2]_2$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	−0.15465 (12)^a	0.06013 (8)	0.12249 (10)	2.76 (5)^b	2.38 (5)	2.68 (5)	0.07 (7)	0.68 (3)	−0.28 (4)
O(1)	−0.3572 (13)	0.0428 (8)	0.2821 (11)	6.2 (8)	6.2 (9)	6.7 (8)	−1.4 (6)	4.2 (6)	−1.1 (4)
O(2)	−0.1890 (10)	0.2582 (7)	0.1325 (10)	4.4 (7)	2.3 (5)	6.2 (6)	0.7 (5)	2.5 (5)	−0.6 (4)
O(3)	−0.1418 (9)	−0.0761 (5)	0.1083 (8)	3.6 (5)	1.6 (4)	3.1 (4)	−0.2 (4)	1.5 (4)	0.0 (3)
N	−0.0073 (10)	0.0453 (6)	0.0150 (8)	2.7 (5)	4.5 (5)	1.6 (5)	−0.2 (5)	0.5 (4)	−0.7 (3)
C(1)	−0.2800 (16)	0.0502 (11)	0.2202 (14)	4.0 (9)	2.5 (8)	4.8 (9)	−1.0 (8)	1.4 (7)	−0.6 (5)
C(2)	−0.1730 (4)	0.1824 (11)	0.1279 (13)	1.5 (7)	3.9 (8)	2.2 (6)	0.1 (7)	0.5 (5)	−0.1 (5)
C(3)	−0.0691 (14)	−0.1012 (9)	0.0337 (12)	2.8 (7)	1.5 (6)	3.0 (8)	0.3 (6)	1.3 (6)	1.2 (4)
C(4)	−0.0671 (13)	−0.1988 (8)	0.0104 (12)	2.0 (7)	1.3 (6)	2.9 (7)	−0.5 (6)	0.2 (5)	−0.1 (4)
C(5)	−0.1140 (15)	−0.2294 (9)	−0.0952 (12)	4.4 (9)	1.8 (7)	2.8 (8)	0.7 (6)	−1.4 (6)	−0.1 (4)
C(6)	−0.1195 (15)	−0.3204 (11)	−0.1213 (12)	4.5 (9)	3.3 (8)	2.7 (7)	0.1 (7)	0.6 (6)	−0.1 (4)
C(7)	−0.0783 (16)	−0.3798 (10)	−0.0344 (15)	4.4 (9)	1.7 (7)	5.0 (9)	−1.5 (7)	0.4 (8)	−0.2 (5)
C(8)	−0.0300 (16)	−0.3510 (11)	0.0708 (14)	3.3 (9)	3.0 (9)	5.2 (10)	0.1 (7)	0.2 (8)	−0.1 (5)
C(9)	−0.0226 (16)	−0.2589 (10)	0.0952 (12)	4.6 (9)	2.8 (8)	2.2 (7)	0.3 (7)	0.5 (6)	−0.1 (4)
H(5)^c	−0.1434	−0.1852	−0.1546	d					
H(6)	−0.1514	−0.3415	−0.1960						
H(7)	−0.0844	−0.4453	−0.0491						
H(8)	−0.0017	−0.3944	0.1285						
H(9)	0.0119	−0.2374	0.1693						

[a] Numbers in parentheses in all tables and in the text are estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal ellipsoid is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [c] The numbering of the hydrogen atoms corresponds to that of the carbon atoms to which they are bound. [d] Hydrogen atoms were assigned isotropic thermal parameters of 4.5 Å^2.

Table III. Bond Distances and Angles

(a) Bond Distances, Å

Rh–C(1)	1.808 (17)	O(3)–C(3)	1.255 (15)
Rh–C(2)	1.820 (16)	C(3)–C(4)	1.470 (18)
Rh–N	2.071 (10)	C(4)–C(5)	1.365 (18)
Rh–O(3)	2.028 (9)	C(4)–C(9)	1.382 (18)
C(1)–O(1)	1.130 (17)	C(5)–C(6)	1.382 (19)
C(2)–O(2)	1.136 (16)	C(6)–C(7)	1.384 (20)
N–N′	1.398 (18)	C(7)–C(8)	1.356 (20)
N′–C(3)	1.309 (16)	C(8)–C(9)	1.393 (20)

(b) Bond Angles, Deg

C(1)–Rh–C(2)	88.6 (7)	Rh–O(3)–C(3)	113.5 (8)
C(1)–Rh–N	169.1 (6)	N′–C(3)–O(3)	122.4 (13)
C(1)–Rh–O(3)	91.5 (6)	N′–C(3)–C(4)	121.5 (12)
C(2)–Rh–N	102.5 (5)	O(3)–C(3)–C(4)	115.9 (11)
C(2)–Rh–O(3)	176.6 (6)	C(3)–C(4)–C(5)	118.9 (13)
N–Rh–O(3)	77.8 (4)	C(3)–C(4)–C(9)	120.6 (13)
Rh–C(1)–O(1)	178.8 (17)	C(4)–C(5)–C(6)	121.8 (13)
Rh–C(2)–O(2)	177.4 (13)	C(5)–C(6)–C(7)	116.9 (14)
Rh–N–N′	110.7 (10)	C(6)–C(7)–C(8)	122.3 (15)
Rh–N–C(3)′	134.6 (9)	C(7)–C(8)–C(9)	120.2 (15)
N–N′–C(3)	114.6 (13)	C(8)–C(9)–C(4)	118.2 (14)

Table IV. Intermolecular Contacts ≤ 3.4 Å in Length[a]

$O(2)\cdots O(2)^{II\,b}$	3.123 (22)	$O(3)\cdots C(3)^{I}$	3.340 (17)
$O(1)\cdots O(1)^{II}$	3.133 (17)	$C(1)\cdots O(2)^{II}$	3.344 (19)
$O(2)\cdots O(2)^{I}$	3.247 (25)	$Rh\cdots Rh^{I}$	3.347 (5)
$O(3)\cdots O(3)^{I}$	3.248 (20)	$C(2)\cdots O(2)^{I}$	3.362 (18)
$C(2)\cdots C(2)^{I}$	3.272 (32)	$C(1)\cdots N^{I}$	3.386 (21)

[a] Contacts involving hydrogen atoms are not included in this table. [b] Superscripts refer to the following symmetry transformations: I, $-\frac{1}{2}-x, y, -z$; II, $-\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$.

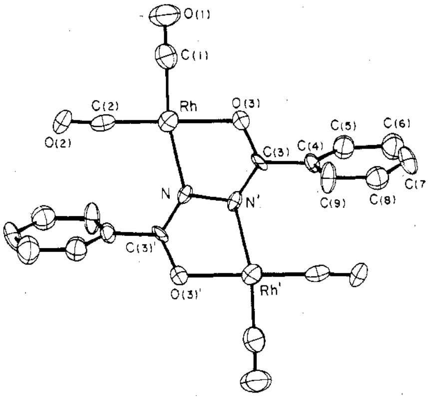

Figure 1. Molecular structure of $[Rh(CO)_2NCOPh]_2$, viewed perpendicular to the metal coordination plane. Primes denote atoms related to those in the asymmetric unit by the molecular center of symmetry at the midpoint of the N–N bond.

are related by a crystallographic center of symmetry at the midpoint of the N–N bond. The bridging $N_2(COPh)_2$ ligand is tetradentate, utilizing all four of its nitrogen and oxygen atoms to form five-membered chelate rings at each Rh atom. The overall structure thus corresponds to II. It is clear from the chemistry of this compound[7] and from its structural details (vide infra) that the bridging ligand is properly visualized as a substituted hydrazido group rather than as a diazene derivative; hence the molecule may be named μ-*N*,*N′*-dibenzoylhydrazido(*N*,*N′*,*O*,*O′*)-bis(dicarbonylrhodium).

The rhodium coordination geometry is essentially square planar, with the major distortion being the N–Rh–O(3) angle of 77.8 (4)°. As can be seen in Table V, the four atoms bound to Rh show small deviations of ca. 0.04 Å from the coordination plane. These deviations describe a slight distortion toward tetrahedral geometry. The Rh–O distance of 2.028 (9) Å is at the short end of the range of Rh–O distances found in square-planar rhodium(I) acetylacetonate complexes; these distances have been found to range from 2.03[13–15] to 2.17 Å.[16]

Table V. Least-Squares Planes

1. $-0.6173X - 0.0092Y - 0.7866Z = -0.0509$[a]

Rh[b]	−0.012[c]	N	−0.036
C(1)	−0.041	O(3)	0.046
C(2)	0.043		

2. $-0.6334X + 0.0722Y - 0.7705Z = 0.0150$

Rh	0.045	C(3)	0.051
N	−0.044	O(3)	−0.066
N′	0.014		

3. $-0.6711X + 0.1314Y - 0.7292Z = 0.0000$

N	0.024	N′	−0.024
C(3)	0.017	C(3)′	−0.017
O(3)	−0.009	O(3)′	0.009
*Rh	0.239		

4. $0.9475X + 0.0364Y - 0.3177Z = -0.8092$

C(4)	−0.008	C(7)	−0.011
C(5)	−0.003	C(8)	−0.000
C(6)	0.013	C(9)	0.010

Angles between Normals to Planes

Planes	Angle, deg	Planes	Angle, deg
1–4	109.6	3–4	113.5
2–4	113.3		

[a] The equations of the planes are expressed with respect to coordinates (*X*, *Y*, *Z*) referred to an orthogonal system (*A*, *B*, *C*) oriented with *A* parallel to *a*, *B* parallel to *b*, and *C* parallel to $A \times B$. [b] All atoms listed were given unit weight in the calculation of all planes, except those marked with an asterisk which were given zero weight. [c] Numbers listed are distances, in Å, to the least-squares plane.

Only a few Rh(I)–N(sp^2) distances are available for comparison with the value of 2.071 (10) Å we observe. In two biimidazole complexes of Rh(I), Rh–N distances ranging from 2.055 (5) to 2.138 (5) Å were found.[17] An 8-hydroxyquinolinatorhodium(I) complex has Rh–N = 2.10 (4) Å.[18] The Rh–C distances of 1.808 (17) and 1.820 (16) Å are equivalent and normal in magnitude.

The atoms of the five-membered metallocyclic ring show deviations of up to 0.06 Å from the mean ring plane (Table V, plane 2). The OCNNCO grouping is more nearly planar (maximum deviation = 0.024 Å) with the metal atom displaced from the plane by 0.215 Å. The phenyl rings are twisted by 66.5° from this ligand plane. Bond distances within the metallocycle suggest substantial electron delocalization over the NCO portion of the ring. The N–C distance of 1.309 (16) Å and the C–O distance of 1.255 (15) Å are both shorter than expected single-bond lengths.[19] On the other hand, the N–N distance of 1.398 (18) Å is essentially a single-bond value. Comparison of these distances with those in the mononuclear Pt(II) complex III (N–C = 1.286 (10) Å, C–O = 1.318 (10) Å, N–N = 1.401 (9) Å)[6] indicate a similar situation in that compound but with a slightly greater degree of delocalization. Although a potential π pathway exists for more extensive delocalization involving the N–N bond, the observed bond distances suggest that this is not a large effect. In a copper(I) complex of dibenzoylhydrazine, a chelating configuration similar to that in III is found with N–C = 1.326 (14) Å, C–O = 1.256 (13) Å, and N–N = 1.435 (12) Å.[20] Several other types of M–N–N–C–O metallocycles are known; some examples of these have recently been tabulated.[6]

As is frequently the case for square-planar d^8 complexes, the dimers display one-dimensional stacking interactions, with short intermolecular contacts. All contacts ≤ 3.4 Å in length not involving hydrogen atoms are tabulated in Table IV and a view of a pair of adjacent dimers is shown in Figure 2. The short contacts may be divided into two groups. Those between molecules related by symmetry transformation II (a centering operation) are incidental contacts between carbonyl groups

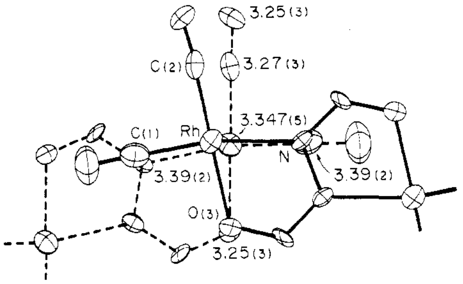

Figure 2. A view of the interaction between an adjacent pair of dimers. Close contact distances corresponding to those for symmetry transformation I in Table IV are shown. An equivalent interaction with a molecule above the plane of the paper involves Rh′ and is generated by the molecular center of symmetry. In this way, the one-dimensional chain is propagated in a "stepwise" fashion with Rh atoms interacting in pairs.

and unrelated to the molecular stacking. The stacked molecules are related by transformation I (a twofold axis) with a Rh–Rh distance of 3.347 (5) Å. This separation is longer than expected for a Rh–Rh single bond but of a magnitude comparable to that of 3.31 Å for the intermolecular Rh–Rh contact in $[Rh(CO)_2Cl]$.[2] Contacts of this magnitude have commonly been associated with weak metal–metal interactions. It is interesting to note that the displacement of the metal atom from the OCNNCO plane is such that the Rh atoms involved in the 3.347 Å separation are displaced toward each other from their respective ligand planes.

The one-dimensional chain formed by these short intermolecular interactions is propagated in a "stepwise" rather than a linear fashion. This is readily apparent from Figure 2 if one recalls that there is a center of symmetry at the midpoint of each N–N bond. Thus the dimer (not shown) above the plane of the paper would have a short metal–metal contact to the rhodium atom at the extreme right of the figure. In principle, there is a pathway for electron delocalization along this chain via the short metal–metal separations and a delocalized π pathway through the bridging ligands. However, this would not be expected to be a large effect because of the length of the Rh–Rh contacts and the apparent lack of extensive delocalization through the N–N bonds. The very small size of the crystals obtained to date precludes any attempt to measure anisotropic conductance properties.

Chemical and spectroscopic evidence indicates that a similar bridging configuration is adopted by the dibenzoylhydrazido ligand in the entire reported series of binuclear Rh(I) and Ir(I) complexes of this ligand.[7] Although these are the first compounds in which this ligand bridges in a bis bidentate fashion, it is evident that the bridging system is a very stable one, since it remains intact through both substitution and oxidation reactions at the metal ion. This bridging group offers potential π pathways for metal–metal interaction; hence it would be of interest to investigate its complexes with paramagnetic metal ions.

Registry No. $[(CO)_2RhN(COPh)]_2$, 59671-04-4.

Supplementary Material Available: Table A, a listing of structure factor amplitudes, and Table B, a tabulation of principal amplitudes of thermal motion (7 pages). Ordering information is given on any current masthead page.

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Crystal Structure of $XeF^+AsF_6^-$ [1]

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Received October 26, 1977

Crystals of $XeF^+AsF_6^-$ are monoclinic, space group $P2_1/n$, $a = 6.308$ (3) Å, $b = 6.275$ (3) Å, $c = 16.023$ (5) Å, $\beta = 99.97$ (5)°, $V = 624.66$ Å^3, $Z = 4$, and $d_x = 3.61$ g cm^{-3}, at 24 °C. X-ray diffraction data were measured with counter methods and Mo Kα radiation. With anisotropic temperature factors for all atoms, $R = 0.033$ for 777 independent reflections ($I > 3\sigma$). The structure consists of ion pairs connected by a bridging fluorine atom into $FXeFAsF_5$ units. The FXeF portion of the molecule is linear (angle = 178.9 (7)°) with Xe–F = 1.873 (6) Å (terminal) and 2.212 (5) Å (bridging). The $FAsF_5$ portion of the molecule is roughly octahedral with cis F–As–F angles ranging from 85.3 (3) to 94.6 (5)°; the five terminal As–F distances range from 1.676 (5) to 1.690 (8) Å and the bridging As–F distance is 1.813 (6) Å. The bridge Xe–F–As angle is 134.8 (2)°.

Introduction

In an earlier paper Sladky et al. described[2] the preparation of the 1:1 XeF_2–AsF_5 complex and showed that it lost AsF_5 readily under vacuum at ordinary temperatures to yield a 2:1 complex. The crystal structure of the 2:1 complex has already been described[3] and is consistent with formulation as the salt $Xe_2F_3^+AsF_6^-$. The structure of the 1:1 complex was of interest to us because of an earlier finding[4] that the structure of the 1:1 XeF_2–RuF_5 complex was consistent with the $XeF^+RuF_6^-$ formulation and our expectation that the formulation of the 1:1 XeF_2–AsF_5 complex would be similar. Moreover, a preliminary study of 1:1 XeF_2–AsF_5 by others[5] had failed to

0020-1669/78/1317-1318$01.00/0