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A Three-Dimensional Interaction Network of δ(M-M) and π(ligand) Electrons. The Crystal Structure of $[Rh_2(mhp)_4](SbCl_6)\cdot 2CH_2ClCH_2Cl$ (mhp = 2-oxy-6-methylpyridine)[1)]

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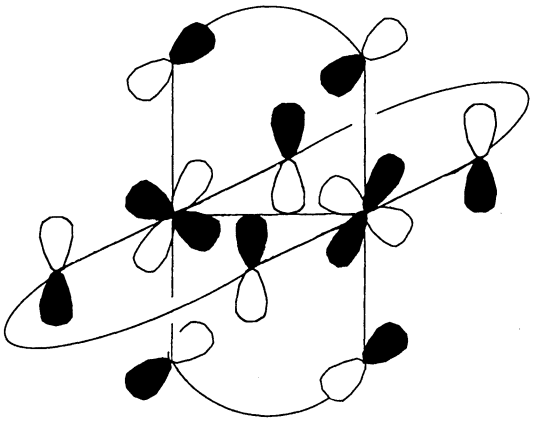
In the crystal of the title compound, the aromatic ring of the cationic radical overlaps with a ring of a neighboring radical. The shortest intermolecular C····C distances are 3.617(5) and 3.646(6) Å. The result of HMO calculations is consistent with intermolecular interaction between the neighboring radicals, resulting in a three-dimensional interaction network involving Rh-Rh δ and aromatic π systems.

The energy of the δ_{RhRh}* orbital in Rh_2^{4+} complexes is largely perturbed by π orbitals of the bridging ligands, which indicates that the δ* orbital is delocalized onto the π systems to a significant extent.[2)] Mixing of an M-M δ orbital and ligand π orbitals has been shown also for $Mo_2(O_2CCH_3)_4$.[3)] Thus the M-M δ-type orbital can conjugate π systems of the bridging ligands arranged around the M-M bond. Expecting a new type of intermolecular interaction system which would be quite difficult to construct by using only organic molecules, we have examined the crystal structure of the salt of the cationic radical, $[Rh_2(mhp)_4]^{+\cdot}$.



The cyclic voltammogram of a dichloromethane solution of $[Rh_2(mhp)_4]$[4)] showed a one-electron chemically reversible oxidation response at $E_{1/2}$ = 0.48 V *vs.* Cp_2Fe/Cp_2Fe^+. The Rh_2^{4+} complex was oxidized to its cationic radical with an equivalent amount of tris(4-bromophenyl)aminium hexachloroantimonate in 1,2-dichloroethane. A frozen dichloromethane solution of the cationic radical showed

an axially symmetric esr absorption of $g_{//}$ = 1.940 (a 1:2:1 triplet of 20.1 × 10^{-4} cm^{-1} due to two equivalent ^{103}Rh nuclei) and $g_{\perp}$ = 2.074 (without hyperfine splitting) at 77 K, which is consistent with the accommodation of the odd electron in the δ_{RhRh}^{*} orbital.[2,5]

Greenish black prismatic crystals of $[Rh_2(mhp)_4](SbCl_6)\cdot 2CH_2ClCH_2Cl$ were grown by slow cooling of a 1,2-dichloroethane solution of the radical salt in a freezer. Since the crystal is quite unstable at room temperature probably due to facile loss of the crystalline dichloroethane, the crystal was mounted quickly on a glass fiber under an ice-cold atmosphere, and its X-ray diffraction data were collected at -150 ± 2 °C.

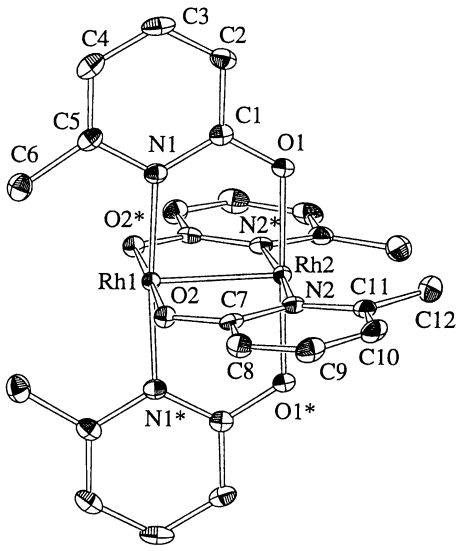


Fig. 1. The geometry and the atom-numbering scheme of $[Rh_2(mhp)_4]^{+\cdot}$. The hydrogen atoms are omitted for clarity. Important interatomic distances and bond angles are: Rh1-Rh2 = 2.3591(7), Rh1-O2 = 1.970(2), Rh2-O1 = 1.986(2), Rh1-N1 = 2.024(3), Rh2-N2 = 2.027(3), O1-C1 = 1.305(4), O2-C7 = 1.302(4), N1-C1 = 1.355(5), N2-C7 = 1.351(5), O1····N1 = 2.307(4), O2····N2 = 2.306(5) Å; Rh2-Rh1-O2 = 90.86(8), Rh1-Rh2-O1 = 90.77(8), Rh2-Rh1-N1 = 87.7(1), Rh1-Rh2-N2 = 87.6(1)°.

Figures 1 and 2 show the structure of the cationic radical and the packing of the cationic radical in the crystal, respectively.[6] The geometry of $[Rh_2(mhp)_4]$ in various crystalline forms, $[Rh_2(mhp)_4]$, $[Rh_2(mhp)_4]\cdot H_2O$, and $[Rh_2(mhp)_4]\cdot CH_2Cl_2$ has been reported.[7] The most significant change in the bond

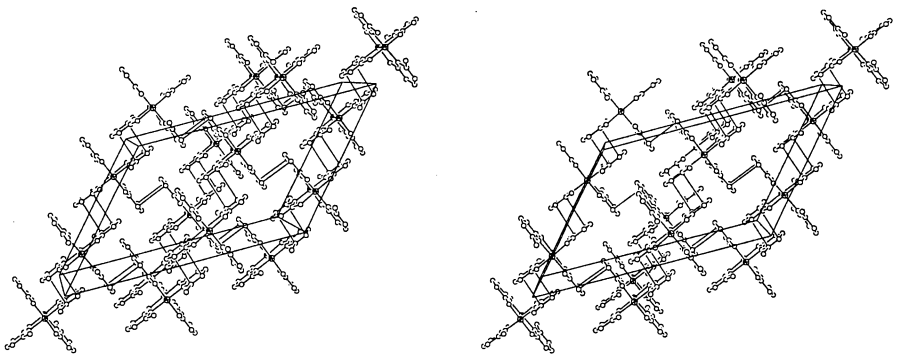


Fig. 2. The stereoview of the packing of $[Rh_2(mhp)_4]^{+\cdot}$ in the crystal of $[Rh_2(mhp)_4](SbCl_6)\cdot 2CH_2ClCH_2Cl$. The crystalline solvent molecules, the hexachloroantimonate anions and the hydrogen atoms are omitted for clarity. The intermolecular contacts between the carbon atoms shorter than 3.7 Å are connected by solid lines.

lengths accompanying the oxidation is the shortening of the average lengths of Rh-N and Rh-O bonds from 2.037(8)—2.053(5)[7] to 2.026(3) Å and from 2.017(5)—2.021(6)[7] to 1.978(8) Å, respectively. This is consistent with the model[2b] in which the electron is removed upon the oxidation from the δ_{RhRh}* orbital with Rh-N and Rh-O π-antibonding character and the orbital is delocalized onto the pyridine ring. Similar intramolecular geometry changes have been reported for $Rh_2\{MeC(O)NH\}_4(H_2O)_2$[8] and $Rh_2(PhNCHNPh)_4(NCMe)$[9] upon their δ_{RhRh}* cationic radical formations. The Rh-Rh bond length of the present cationic radical is 2.3591(7) Å, which is in the range of the corresponding length of the neutral mother molecule in various type of crystals, 2.359(1)—2.370(1) Å,[7] although the electron in the δ_{RhRh}* orbital was removed upon the oxidation. The antibonding character of the δ_{RhRh}* orbital is too ineffective to shorten the Rh-Rh length upon the removal of the electron from this orbital.

In the crystal, pyridine rings of the ligands are overlapping on rings in nearest neighbors. There exist two modes of intermolecular ring-ring overlap. The overlapping rings are crystallographically parallel to each other (inversion center) in both types of the overlap. In the first one, C4 and C5 atoms are lying on C5 and C4 atoms in the neighboring radical, respectively, and the inter-plane distance is 3.649 Å. In the other mode, C8 and C10 atoms are located on the C10 and C8 atoms of the nearest neighbor, respectively, and the inter-plane separation is 3.606 Å. The intermolecular C4·····C5 and C8·····C10 distances are 3.646(6) and 3.617(5) Å, respectively. Although these distances are most separated ones as for intermolecularly interacting aromatic carbon atoms, HMO calculations show that C4, C5, C8 and C10 are the sites where the HOMO of the anion of the bridging ligand has the largest densities (Fig. 3). This HOMO of the bridging ligand anion is the orbital that is allowed to mix into the δ_{RhRh}* odd electron orbital. Thus we propose that there exists intermolecular SOMO-SOMO interaction in this crystal. The interesting point of the present crystal structure is that four aromatic π systems located around the Rh-Rh bond are intramolecularly conjugated through a metal-metal δ-type orbital, and the intermolecular π-π interaction results in a three dimensional interaction network. We are now trying to prepare crystals stable enough to examine their magnetic susceptibilities and electronic spectra.

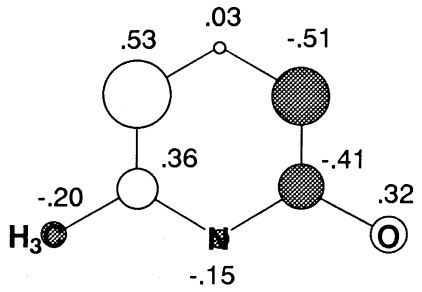


Fig. 3. The HOMO of 2-oxo-6-methylpyridine anion calculated with HMO method with parameters recommended by Streitwieser.[10] The numbers show the coefficients of the π atomic orbitals.

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References

1) Dedicated to the late Professor Hiroshi Kato.

2) a) T. Kawamura, H. Katayama, and T. Yamabe, *Chem. Phys. Lett.*, **130**, 20 (1986); T. Kawamura, H. Katayama, H. Nishikawa, and T. Yamabe, *J. Am. Chem. Soc.*, **111**, 8159 (1989).

3) D. L. Lichtenberger, C. D. Ray, F. Stepniac, Y. Chen, and J. H. Weaver, *J. Am. Chem. Soc.*, **114**, 10492 (1992).

4) M. Berry, C. D. Garner, I. H. Hillier, A. A. MacDowell, and W. Clegg, *J. Chem. Soc., Chem. Commun.*, **1980,** 494.

5) T. Kawamura, K. Fukamachi, T. Sowa, S. Hayashida, and T. Yonezawa, *J. Am. Chem. Soc.*, **103**, 364 (1981).

6) a) Crystal data: $Rh_2C_{28}H_{32}N_4O_4SbCl_{10}$, M = 1170.68, size 0.15 × 0.15 × 0.4 mm^3, monoclinic, $C2/c$(No. 15), a = 24.036(2), b = 13.412(1), c = 15.841(1) Å, β = 130.312(3)°, V = 3894.2(6) Å^3, Z = 4, ρ_{calc} = 1.828 g cm^{-3}, μ = 21.07 cm^{-1}; Data collected with Mo-Kα(λ = 0.71069 Å) radiation on a Rigaku AFC-7R diffractometer equipped with a Rigaku XR-TCS-2-050 temperature controller; scan rate 32°/min; 4° < 2ϑ < 55°; 4772 measured intensities, 3412 with $I > 3\sigma(I)$. The structure was solved by Patterson map method› an absorption correction using the DIFABS technique [N. Walker and D. Stuart, *Acta Crystallog.*, **A39**, 158 (1983)] was applied (T = 0.92 - 1.07), and the non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically with full-matrix least-squares method (288 variables): R = 2.7, R_W = 2.3%.

7) W. Clegg, *Acta Crystallog.*, **B36**, 2437 (1980); F. A. Cotton and T. R. Felthaouse, *Inorg. Chem.*, **20**, 584 (1981); W. Clegg, C. D. Garner, L. Akhter, and M. H. Al-Samman, *Inorg. Chem.*, **22**, 2466 (1983).

8) I. B. Baranovskii, M. A. Golubnichaya, L. M. Dikareva, A. V. Rotov, N. Shchelokov, and M. A. Porai-Koshits, *Russ. J. Inorg. Chem.*, **31**, 1652 (1986); M. Q. Ahsan, I. Bernal, and J. L. Bear, *Inorg. Chem.*, **25**, 260 (1986).

9) J. L. Bear, C. -L. Yao, R. S. Lifsey, J. D. Korp, and K. M. Kadish, *Inorg. Chem.*, **30**, 336 (1991).

10) A. Streitwieser, Jr, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, NY (1961), p135.

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