Eclipsed Cofacial Dimers of Metal Complexes Containing d^7–d^7 and d^8–d^8 Metal Bonds. Crystal Structure of Bis[bis{(phenanthrene-9,10-diamin)ylato}cobalt(II)] and Bis[{(2,3-dicyanoethenediamin)ylato}dicarbonylrhodium(I)]

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Two novel crystal structures containing the eclipsed conformation of diaminylato type ligands and metal–metal bonds are described; bis[bis{(phenanthrene-9,10-diamin)ylato}cobalt(II)] contains a Co^{II}–Co^{II} bond [2.689(1) Å] and two δ bonds between two pairs of parallel (phenanthrene-9,10-diamin)ylato ligands and bis[{(2,3-dicyanoethenediamin)ylato}dicarbonylrhodium(I)] contains a Rh^{I}–Rh^{I} bond [2.833(2) Å] and one δ bond between a pair of parallel (2,3-dicyanoethenediamin)ylato ligands.

π–π interactions between highly conjugated molecules, *e.g.* the ttf-tcnq (ttf = tetrathiafulvalene, tcnq = 7,7,8,8-tetracyano-*p*-quinodimethane) complex, play important roles in their electron transport processes[1] but only a few examples of strongly attractive bonding interactions of these molecules have been reported.[2–4] Two requirements are necessary for these attractive interactions—the close cofacial approach of the planar molecules and the odd electron population attributed to π or π* orbitals of the molecules. Here we report two novel crystal structures of metal complexes of diaminylato-type ligands which contain synergic metal–metal bonds and ligand–ligand bonds.

The blue binuclear complex $[Co(phda)_2]_2$ **4**† was synthesized by the reaction of 9,10-diaminophenanthrene **1** and $Co(OAc)_2$ in dimethylformamide (dmf) followed by air oxidation. Suitable single crystals were crystallized from solution solvated with dmf. The structure of **4** consists of discrete dmf-solvated dimeric complexes, $[Co(phda]_2]_2(dmf)_2$ (Figs. 1 and 2).‡ The crystallographic centre of inversion is located between two cobalt atoms. Complex **4** has several uncommon features. First, it contains a short Co^{II}–Co^{II} bond [2.689(1) Å], which is shorter than those in $[Co_2^{II}(CN)_{10}]^{6-}$ (2.794 Å)[5] and $[Co_2^{II}(CNMe)_{10}]^{4+}$ (2.734 Å),[6] but longer than

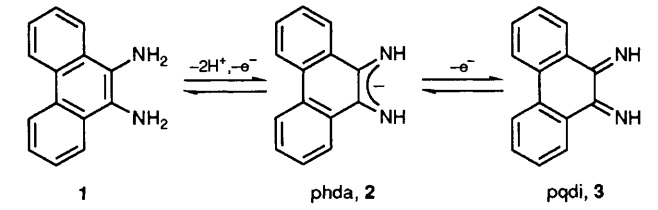
† *Spectral data* for complex **4**: diamagnetic, δ [$(CD_3)_2SO$] 13.43 (NH), 7.7–9.1 (aromatic CH); ν_{N-H} 3238 cm^{-1}; λ_{max}/nm 767 (ε/dm^3 mol^{-1} cm^{-1} 1.82×10^4), 592 (1.34×10^4) and 352 (1.98×10^4). For complex **8**: diamagnetic, δ [$(CD_3)_2SO$] 10.34 (NH, br); ν_{N-H}/cm^{-1} 3277, 3237, ν_{C-N} 2220, 2211, ν_{C-O} 2096, 2081; λ_{max}/nm 370 (ε/dm^3 mol^{-1} cm^{-1}, 8.22×10^3), 310 (sh, 1.00×10^4).

‡ *Crystal data* for $[Co(phda)_2]_2(dmf)_2$: monoclinic, space group $P2_1/n$, a = 9.980(4), b = 15.789(3), c = 15.826(3) Å, β = 96.08(4), V = 2480(1) $Å^3$, D_m = 1.46, D_c = 1.459 g cm^{-3}, Z = 2; CAD4 diffractometer with graphite-monochromated Mo-Kα radiation, Ψ scan absorption correction was made; 4356 unique reflections ($2\theta < 50°$) were measured and 3309 reflections with $I > 2\sigma(I)$ were used in the refinement. The refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms (356 variables) converged to R = 0.036 and R_w = 0.036.

For $[Rh(dced)(CO)_2]_2$: monoclinic, space group $P2_1/n$, a = 6.865(2), b = 35.467(6), c = 13.969(2) Å, β = 95.50(2)°, V = 3386(1) $Å^3$, D_m = 2.10, D_c = 2.08 g cm^{-3}, Z = 8; CAD4 diffractometer with graphite-monochromated Mo-Kα radiation. Ψ scan absorption correction was made; 5936 unique reflections ($2\theta < 50°$) were measured and 2483 reflections with $I > 2\sigma(I)$ were used in the refinement. The refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms (469 variables) converged to R = 0.042 and R_w = 0.031. Atomic coordinates, bond lengths and angles, and thermal parameters of these two compounds have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

that in $[Co_2(dced)_4]^0$ [2.633(3) Å].[4] The Co atom is displaced 0.186(1) Å from the plane formed by the four N atoms toward one another. Secondly, the four phda ligands are arranged in an eclipsed fashion forming two pairs of cofacial ligands which are separated by only 3.0 Å. Thirdly, it contains a short Co–N bond [av. 1.847(2) Å] and delocalized C–N [av. 1.331(4) Å], C–C [av. 1.429(4) Å] bonds in the five-membered chelate ring. Both features indicate the ligands to be in the diaminylato state.[7–9] These structural features are identical to those of $[Co_2(dced)_4]^0$.[4] Thus, the same bonding scheme is proposed, namely that there are a Co^{II}–Co^{II} σ-bond and two δ-type§ bonds between two pairs of parallel ligands in this cofacial dimeric complex.

The dark-green binuclear complex $[Rh^I(dced)(CO)_2]_2$ **8**† was synthesized by the reaction of damn **5** and $[RhCl(CO)_2]_2$ in acetonitrile followed by air oxidation. Suitable single crystals were slowly formed from solution. The structure of **8** consists of one-dimensional columns. Two independent dimeric complex molecules stacked along the crystallographic *a* axis form columns with metal atoms located atop one another (Figs. 3 and 4).‡ Rhodium atoms that form the core of a column are not perfectly aligned above one another with Rh–Rh distances 2.822(2), 2.843(2) Å within dimers, 4.081(2), 4.109(2) Å between dimers, and Rh–Rh···Rh angles



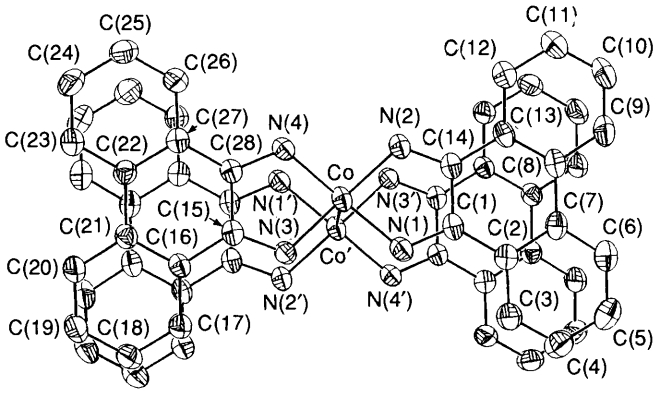


Fig. 1 ORTEP drawing of the $[Co^{II}(phda)_2]_2$ Pertinent bond lengths (Å) and angles (°): Co–Co' 2.689(1), Co–N(1) 1.840(2), Co–N(2) 1.851(2), Co–N(3) 1.852(2), Co–N(4) 1.844(2), C–N ranging from 1.317(4) to 1.341(4) av. 1.331, C(1)–C(14) and its equivalents av. 1.429, C(1)–C(2) and its equivalents av. 1.445, C(2)–C(3) and its equivalents av. 1.409, C(2)–C(7) and its equivalents av. 1.414, C(3)–C(4) and its equivalents av. 1.370, C(4)–C(5) and its equivalents av. 1.378, C(5)–C(6) and its equivalents av. 1.375, C(6)–C(7) and its equivalents av. 1.400, C(7)–C(8) and its equivalents av. 1.472; Co'–Co–N(1) 82.4(1), Co'–Co–N(2) 102.6(1), Co'–Co–N(3) 88.9(1), Co'–Co–N(4) 108.7(1), N(1)–Co–N(2) 81.9(1), N(1)–Co–N(3) 97.1(1) and N(1)–Co–N(4) 168.7(1)

§ The term δ-type bond is applied because two nodal planes are present.

167.74(4), 161.55(4)° for A and B dimers, respectively. Within the dimer, there are also several notable features. First, it contains a Rh^I–Rh^I bond [av. 2.833(2) Å]. The Rh atoms are displaced 0.14 Å from the plane formed by the four coordinated atoms (N_2C_2) toward one another. The d^8–d^8 metal–metal bonds are not common, although several have been characterized.[2,3,10] Secondly, the two dced ligands are arranged in an eclipsed conformation and are separated by 3.0 Å. The dced ligand is bent only 3° (av.) outward from the coordination plane. Instead, the CO ligands (plane defined by two CO ligands) are bent 9° (av.) outward from the coordination plane to minimize the non-bonding interaction. These findings indicate the attractive interaction between the dced ligands. Thirdly, the bond pattern of dced ligands is typical of coordinated diaminylato ligands with an average C–N length 1.33(2) Å and C–C length 1.38(2) Å. This bond pattern is identical with those of $[Ni(dced)_2]$[11] and $[Pt(dced)_2]$.[12] In order to account for these structural

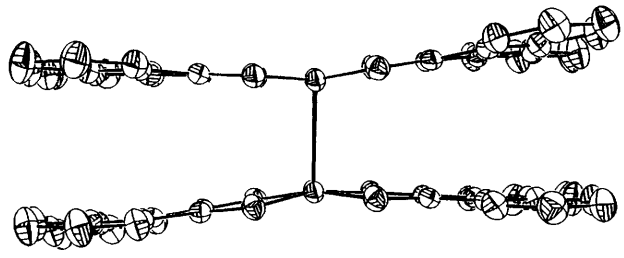


Fig. 2 Another view of $[Co_2(phda)_4]$ illustrating the eclipsed cofacial geometry of the dimer

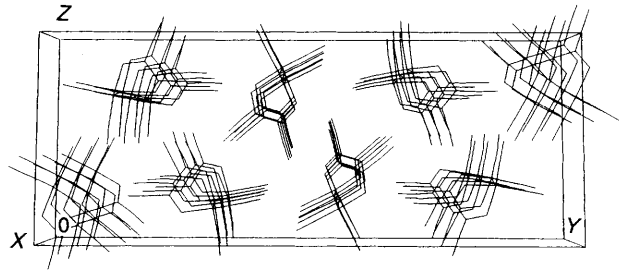


Fig. 3 A view of contents of three unit cells of $[Rh(dced)(CO)_2]_2$ illustrating the stacked nature of the dimers

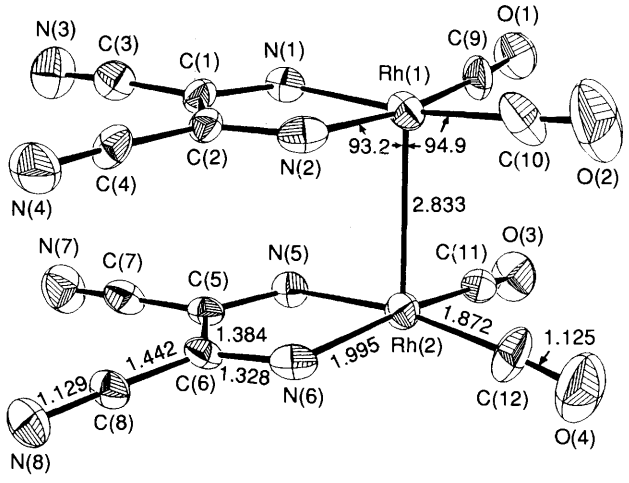


Fig. 4 ORTEP drawing of one of two crystallographic independent dimers $[Rh(dced)(CO)_2]_2$. The bond distances are the average values of chemically equivalent bonds. Estimated standard deviations: 0.01–0.02 Å. Pertinent average bond angles (°): N–Rh–N 78.0(4), C–Rh–C 90.5(7), N–Rh–C_{cis} 95.2(6) and N–Rh–C_{trans} 169.7(6).

features, we propose that, there is one Rh^{I}–Rh^{I} bond and one δ bond between the pair of dced ligands.

Lange *et al.* have reported the structure of closely related [3,6-di-*tert*-butyl-(benzene-1,2-dihydroxy)ato]dicarbonylrhodium(I) **9**.[13] There are two significant differences between structures **8** and **9**. Compound **8**, $[\{Rh^{I}(dced)(CO)_2\}_2]$ forms a diamagnetic dimer, but compound **9** remains monomeric with a complicated magnetic interaction. Both compounds have columnar structures, **8** has an eclipsed conformation within the dimer and between dimers; instead, **9** has a staggered geometry between the monomers.

The reason that the $[Co(phda)_2]$ and $[Co(dced)_2]$ complexes form diamagnetic dimers, whereas $[Co(bnda)_2]$ and $[Co(npda)_2]$ bnda = (benzene-1,2-diamin)ylato, npda = (naphthalene-2,3-diamin)ylato][7,8] are paramagnetic monomers is unknown. A similar question can be raised about the Rh complexes. The dimer formation may be related to the energy level of diimine π* orbitals. Detailed molecular orbital calculations are in progress.

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