Chelate Ligands

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Establishing the Chelating α-Azocarbonyl Function in π-Acceptor Ligands

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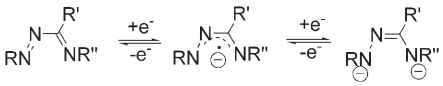
In memory of Hans Bock

Four-center two-step redox systems [see Eq. (1)] with coordinating heteroatoms in 1,4-positions have long played a prominent role in coordination chemistry as potentially noninnocent[1] chelate ligands. Reducible α-diimines (E, E′ = NR) including 1,4-diazabutadienes,[2] *o*-quinonediimines[3] or "polypyridines" of the 2,2′-bipyridine or 1,10-phenanthroline type[4] have thus been studied particularly under the aspect of light-induced charge transfer, while the more easily reduced α-diketones and especially *o*-quinones (E, E′ = O)[5] can exhibit the phenomenon of redox isomerism ("valence tautomerism") in their transition-metal complexes.[6] The related complexes of α-dithiolene ligands (E, E′ = S), long known[7] and recently reinvestigated,[8] are often cited as prototypes of coordination compounds with partially covalent metal–donor bonds.

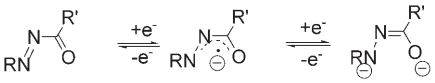
(1)

Mixed systems E ≠ E′ are also known in the form of, for example, α-iminoketones[9] (E = NR, E′ = O, especially *o*-quinonemonoimine derivatives[1a]), as α-iminopyridines[10] or as α-azoimines, RNNC(R′)NR″ [Eq. (2)], involving the strongly π-electron-accepting azo function[11] and heteroaromatic components such as pyridines or tetrazines.[12] Recently, complexes of reduced α-azoimines were obtained from the ring opening of 1,2,4,5-tetrazines.[13]



(2)

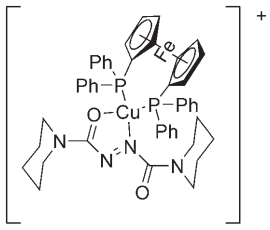
The hitherto neglected combination RNNC(R′)O [Eq. (3)], coupling π-electron-deficient[14] carbonyl and azo functions, has been observed and structurally established in doubly and singly reduced form;[15] however, the unreduced group N=N–C=O was not yet described as part of an isolated metal chelate system.



(3)

Herein, we report spectroscopic and structural evidence for a first such case by example of the heterodinuclear compound $[Cu^{I}(adc\text{-}pip)(dppf)](BF_4)$, (**1**)$(BF_4)$, obtained as a deep purple material by reacting azodicarboxylic acid dipiperidide (adc-pip) with $[Cu(dppf)(CH_3CN)_2](BF_4)$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene).[16a] Azodicarbonyl compounds $[R(O)CNNC(O)R]^n$ are not only valuable reagents in organic synthesis[17] but also unique noninnocent ligands[15] that tend to coordinate in a bridging manner, while the organometallic dppf is a well-used ligand for structure fixation, electron transfer, and catalysis.[18]

The molecular structure of $\mathbf{1}^+$ (Figure 1)[19] shows how one of the N=N–C=O functions chelates the copper(I) center of



$\mathbf{1}^+$

heterodinuclear $[Cu(dppf)]^+$ without being reduced to the monoanionic (radical) or dianionic form. This assignment follows not only from the composition of the material but also from the analysis of the strongly alternating intrachelate bonds with lengths $d_{N=N} = 1.258(7)$, $d_{C-N} = 1.466(8)$, and $d_{C=O} = 1.234(7)$ Å. Apparently, there is relatively little π back-donation from this form of copper(I), which might otherwise lengthen the double bonds and shorten the single bond or even cause an eventual reduction of the ligand. With $d_{Cu-N} = 1.990(5)$ and $d_{Cu-O} = 2.170(4)$ Å the metal chelation is rather asymmetric, in agreement with the different basicities of N and O; the dihedral angle between the P1-Cu-P2 and O1-Cu-N2 planes is 87.14° so that the configuration at the metal

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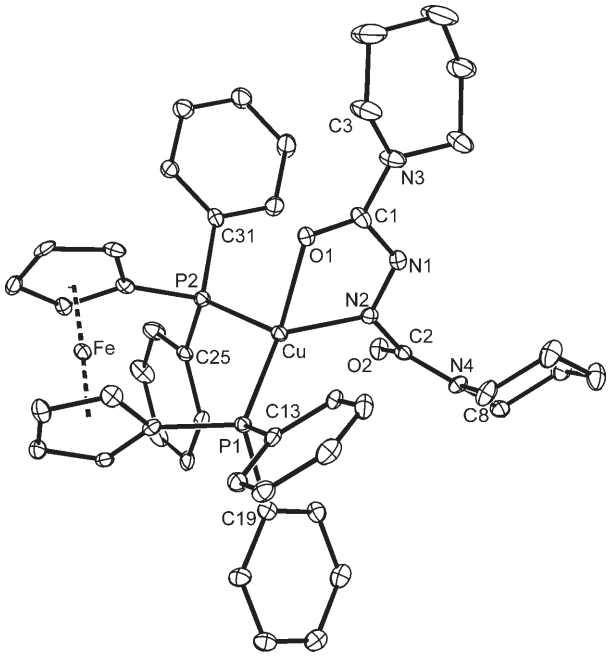

Figure 1. Molecular structure of the cation in the crystal of (**1**)-$(BF_4)\cdot H_2O$. Selected bond lengths [Å] and angles [°]: Cu–P1 2.228(2), Cu–P2 2.254(2), Cu–N2 1.990(5), Cu–O1 2.170(4), C1–O1 1.234(7), C1–N1 1.466(8), N1–N2 1.258(7), N2–C2 1.470(7), C2–O2 1.216(7), Cu–Fe 4.048; P1-Cu-P2 109.85(6), P1-Cu-N2 128.01(15), P1-Cu-O1 116.66(12), P2-Cu-N2 115.71(14), P2-Cu-O1 104.02(12), N2-Cu-O1 75.29(17).

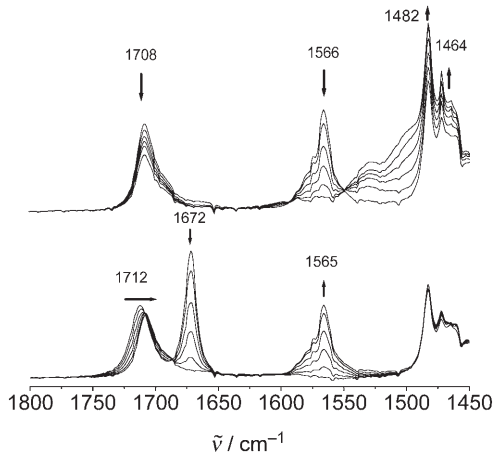

Figure 2. IR spectroelectrochemistry of the conversion $\mathbf{1}^+ \rightarrow \mathbf{1}^\bullet$ (bottom) and $\mathbf{1}^\bullet \rightarrow \mathbf{1}^-$ (top) in CH_2Cl_2/0.1 M Bu_4NPF_6.

center can be described as distorted tetrahedral. The stability of the situation with unreduced N=N–C=O is probably favored by the rigidity of the heterodinuclear $[Cu(dppf)]^+$ complex fragment.

The closely related complex $[Cu(adc\text{-}NMe_2)(dppf)](BF_4)$, (**2**)$(BF_4)$, was obtained using azodicarboxylic acid bis(dimethylamide).[16] In both cases, attempts to obtain tetranuclear Cu_2Fe_2 complexes[15] were unsuccessful, possibly owing to steric hindrance. The external addition of an electron to $\mathbf{1}^+$ at −0.87 V versus ferrocene/ferrocenium ($Fc^{+/0}$) in CH_2Cl_2/0.1 M Bu_4NPF_6 at −70 °C[20] produces a neutral radical complex $[Cu^I(adc\text{-}pip^{\bullet-})(dppf)]$, as evident from a partially structured EPR signal of approximately 16 mT total width at $g = 2.0073$. Most instructively, the spectroelectrochemical monitoring of the reduction by carbonyl vibrational spectroscopy (Figure 2) shows a negligible shift (1712 → 1708 cm^{-1}) for the uncoordinated carbonyl group but a considerable low-energy shift from 1672 to 1565 cm^{-1} for the coordinated C=O function.[16b] The second reduction at −1.76 V also occurs in the chelate ring [Eq. (3), R′ = C(O)pip], as evident from the shift of $\tilde{\nu}_{CO(coord.)}$ to 1482 cm^{-1} and the stationary 1708 cm^{-1} band (Figure 2), still assigned to $\tilde{\nu}_{CO}$ of the uncoordinated carbonyl group.

The reduction steps of (**1**)(BF_4) are accompanied by UV/Vis spectroscopic changes, showing first a bathochromic shift of the metal-to-ligand charge transfer (MLCT, $d(Cu^I) \rightarrow \pi^*$) band from 520 nm ($\varepsilon = 2550\ M^{-1}cm^{-1}$) to 640 nm ($\varepsilon = 1400\ M^{-1}cm^{-1}$)[16b] and then, in the second reduction step, the disappearance of any absorption in the visible owing to full occupation of the π acceptor molecular orbital.

The oxidation of heterodinuclear $(\mathbf{1}^+)(BF_4)$ at +0.37 V versus $Fc^{+/0}$ occurs reversibly at the ferrocene function, as confirmed by virtually unchanged carbonyl stretching bands in the IR spectrum and by the emergence of the typical[21] ferrocenium absorption shoulder at about 770 nm in addition to the hypsochromically shifted MLCT band (520 → 462 nm, $\varepsilon = 3170\ M^{-1}cm^{-1}$).[16b]

We have thus shown that the heterodinuclear complex cation $[Cu(dppf)]^+$ can engage in charge transfer relative to the strongly π-accepting chelate system N=N–C=O without causing full electron transfer, thus allowing for the first time to study the spectroscopy and structure of an unreduced α-azocarbonyl metal complex. We assume that both the steric hindrance and the donor effect of the dialkylamino substituents at the carbonyl carbon atoms are responsible for this result. Other potential chelate ligands containing the RN=N–C(R′)=O function may thus be devised to serve as a new kind of π acceptor in coordination chemistry.

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[16] a) The complexes were prepared by the following general procedure (details are given for (**1**)(BF_4)). A mixture of $[Cu(dppf)(CH_3CN)_2]BF_4$ (0.050 g, 0.714 mmol) and azodicarboxylic dipiperidide (adc-pip) (0.020 g, 0.792 mmol) in dry dichloromethane (20 mL) was stirred at room temperature for 8 h under argon atmosphere, which resulted a dark violet solution. On removal of the solvent under reduced pressure, a dark solid was obtained, which was washed with hexane and dried in vacuo. The deep purple solid was recrystallized from dichloromethane/hexane (1:5). Yield 41 mg (55 %). Elemental analysis (%) calcd for $C_{46}H_{48}CuF_4FeN_4O_2P_2{\cdot}CH_2Cl_2$: C 54.18, H 4.84, N 5.38; found: C 55.62, H 5.10, N 5.49 %; ^{1}H NMR (CD_2Cl_2, 200 MHz): $\delta = 1.61$–1.82 (m, piperidide,), 3.42 (m, piperidide), 3.75 (m, piperidide), 4.32 (s, 4H, Cp), 4.52 (s, 4H, Cp), 7.35 ppm (m, 20H, Ph); ^{31}P NMR (CD_2Cl_2, 200 MHz): $\delta = -6.87$ ppm; IR (CH_2Cl_2): 1672 (coordinated C=O), 1712 cm^{-1} (free C=O). For complex (**2**)(BF_4): yield 45 mg (65 %); Elemental analysis (%) calcd for $C_{40}H_{40}CuF_4FeN_4O_2P_2{\cdot}CH_2Cl_2$: C 51.20, H 4.40, N 5.82; found: C 50.77, H 4.46, N 5.87; ^{1}H NMR (CD_2Cl_2, 200 MHz): $\delta = 2.98$ (s, 6H, CH_3), 3.16 (s, 6H, CH_3) 4.32 (s, 4H, Cp), 4.40 (s, 4H, Cp), 7.42 ppm (m, 20H, Ph); ^{31}P NMR (CD_2Cl_2, 200 MHz): −7.58 ppm; IR (CH_2Cl_2) 1686 (coordinated C=O), 1716 cm^{-1} (free C=O); b) Spectroelectrochemical data for the system $\mathbf{2}^+/\mathbf{2}$: IR (CH_2Cl_2/0.1 M Bu_4NPF_6) 1716→1714 cm^{-1} ($\nu_{CO(uncoord.)}$), 1686→1585 cm^{-1} ($\nu_{CO(coord.)}$); UV/Vis (CH_2Cl_2/0.1 M Bu_4NPF_6) 521→626 nm. System $\mathbf{2}^+/\mathbf{2}^{2+}$: UV/Vis ($CH_2Cl_2$/0.1 M Bu_4NPF_6) 521→472 nm. The second reduction **2**/$\mathbf{2}^-$ was not sufficiently reversible for spectroelectrochemistry.

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[19] a) Single crystals of **1**·H_2O were grown by slow diffusion of hexane into a dichloromethane solution and were measured using $Mo_{K\alpha}$ radiation (0.71073 Å). $C_{46}H_{48}BCuF_4FeN_4O_3P_2$, $M_r = 937.02\ g\,mol^{-1}$, monoclinic, space group $P2_1/n$, $a = 18.9131(12)$, $b = 9.3832(6)$, $c = 26.1565(12)$ Å, $\beta = 106.199(4)°$, $V = 4457.6(5)$ Å^3, $T = 100(2)$ K, $Z = 4$, $\rho_{calcd} = 1.450\ g\,cm^{-3}$, $\mu = 0.937\ mm^{-1}$, $2\theta_{max} = 56.52°$, 8692 independent reflections (R(int) = 0.0005), $R1 = 0.0840$, $wR2 = 0.1967$ (for 6280 reflections with $I \geq 2\sigma(I)$), $R1 = 0.1229$, $wR2 = 0.1784$ (all data), GOF (F^2) = 1.120, data/restraints/parameter = 8692/0/555, largest differential peak and hole 1.808 and −1.520 e Å^{-3}. The structure was solved and refined by full-matrix least-squares on F^2 using SHELX-97 (SHELXTL). Hydrogen atoms were included in the refinement process as per the riding model. CCDC-682007 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif; b) G. M. Sheldrick, SHELX-97 Program for Crystal Structure Solution and Refinement, University of Göttingen, Göttingen, Germany, **1997**.

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