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LETTERS

What Does "Through-Bond Coupling" Mean? Observations on Simple Donor−Acceptor Systems

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A series of covalently linked, transition-metal donor/acceptor complexes are described in which the net donor−acceptor coupling matrix element, H_{DA}, is independent of the extent of coupling between the donor and the bridging ligand. The bridging ligand in these complexes is a transition-metal dicyano complex with a tetraaza aliphatic nonbridging ligand, *cis*- or *trans*-M(MCL)$(CN)_2^+$ for M = Rh(III), Co(III), or Cr(III), donor = $Ru(NH_3)_5^{2+}$, and the acceptor = $Ru(NH_3)_5^{3+}$. The electronic coupling (and electron delocalization) between the donor and the central atom (M) of the bridging ligand varies from $H_{DL} \approx 10^3$ to $\sim 3 \times 10^3$ cm^{-1} through the series of M(MCL)$(CN)_2^+$-bridged complexes, and this variation has an effect on the energy of the Ru(II)/Ru(III) CT absorption maximum, which is expected from perturbational mixing of these electronic states. However, the usually correlated superexchange contribution to H_{DA} is not observed and appears to be less than about 10% of the contribution predicted. This is in contrast to observations on related complexes with pyridyl-type bridging ligands. The unusual behavior can be a consequence of the dependence of D/A electronic coupling on the CN^- vibrational distortions and the mixing of the two Ru(II)/Ru(III) electron-transfer states with the BL state promoted by in-phase and out-of-phase combinations of CN^- stretches. Such an approach predicts very little superexchange coupling when there is little electron delocalization onto the bridging ligand and requires that H_{DA} be a strong function of the electron-transfer coordinates.

Electronic coupling (H_{DA}) between an electron transfer donor (D) and acceptor (A) is a complex issue of considerable fundamental importance.[1−7] It is a major factor in the efficiency of long-range electron transfer in biological systems, the conductivity or efficiency of "molecular wires" and other potential molecular devices, and in the understanding of the fundamental aspects of any electron-transfer-based process.[1−16] Accounting for the bridging ligand contributions to H_{DA} in linked D/A systems has been a major concern for much of this work.[1−5,8−12] In this report, we describe some dramatic evidence that linker-mediated vibronic[17,18] effects can alter the patterns of H_{DA} in simple covalently linked D/A complexes. These observations should provide important criteria for evaluating the range of validity of theoretical models for D/A electronic coupling and should also be important considerations in strategies for designing molecular-level devices.

Experimental evaluations of H_{DA} have generally been based on the oscillator strengths of D/A charge transfer (CT) absorption bands, from the fits of electron-transfer rate data to kinetic models, or variations in electrochemical behavior.[1,2,8−11,13] Relatively simple models are often used; e.g., that H_{DA} decreases as a monotonic, usually exponential function of the spatial separation (or "path length") along a covalent connector.[1,2,11−15] Such approaches have successfully described the behavior of a large number of systems. However, there is evidence that simple models are not always useful: (a) the D/A separation distance, r_{DA}, is a parameter dependent on the distribution and polarization of the electron density of the initial and final

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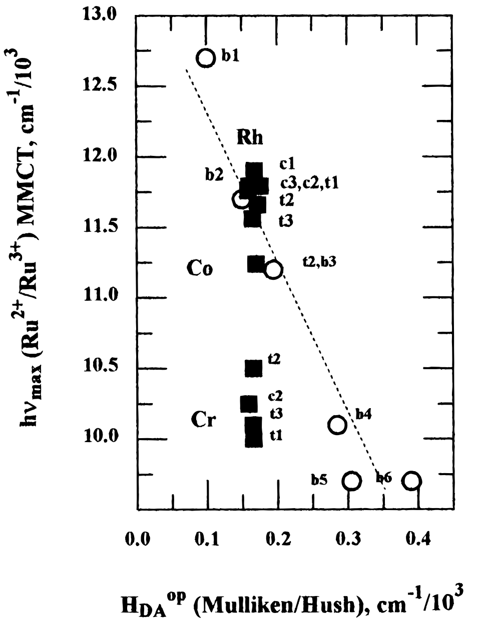

Figure 1. Comparisons of the variations in $h\nu_{max}$(IV) with those for the electronic matrix element (H_{DA}) inferred from the oscillator strength of the IV absorption band for pyridyl bridges (○) and M(MCL)(CN)$_2{}^+$ bridges (■); see ref 30 for identity of bridging ligands.

states;[19−22] (b) theoretical models have suggested that H_{DA} may not decay uniformly from one linker to the next;[6,23] (c) some molecular systems exhibit “quantum interference” effects;[24] and (d) values of H_{DA} based on different measurements on the same molecule are sometimes inconsistent.[17,25,26]

In a large number of molecular systems electronic coupling has been found to alter the molecular properties in patterns which are consistent with the arguments of Hush[7] and of Mulliken.[19] Most notably, this has been the case for complexes of the type $[Ru(NH_3)_5]_2(BL)$ in which $H_{DA} < \sim 200$ cm^{-1} [8−10,27] and have often served as model systems with which to test the validity of the theories. We find very different patterns when BL is a dicyanometallo complex with an aliphatic tetraazamacrocyclic nonbridging ligand (BL = *cis*- or *trans*-M(MCL)(CN)$_2{}^+$, where M = Co(III), Rh(III), or Cr(III)). In these complexes, the oscillator strength of the intervalence charge transfer (IVCT) transition and H_{DA} are independent of the Ru(II)/M(III) coupling (H_{DL}), even when this coupling is strong enough to give rise to an intense donor/bridging-ligand charge-transfer absorption (DLCT) absorption, as in the complexes with M = Cr(III) for which $H_{DL} \approx 3 \times 10^3$ cm^{-1}.[17] Thus, we find that $\epsilon_{max}(av) = 121 \pm 16$ for the *cis*- and *trans*-M(MCL)(CN)$_2{}^+$-bridged complexes, independent of M. This unusual behavior contrasts dramatically to that of IVCT transitions in complexes with BL being a substituted 4,4′-bipyridine-type of ligand by Taube and co-workers.[27]

The mixing of the two electron-transfer states with the higher energy CT state(s) (designated **c**) of the bridging ligand (i.e., for $\psi_i = \psi_i{}^\circ + \alpha_{ij}\psi_j{}^\circ$ where $\alpha_{ij} = H_{ij}/E_{ij}$), which gives rise to $H_{DA}{}^s$, eq 1,[1,12] also results in the stabilization of the lower energy electron-transfer states (**g** and **e**) by $\epsilon_{ij} = \alpha_{ij}2E_{ij}$ (see Figure 2).[18] It is usually assumed that $H_{ec} = H_{gc} \cong (0.0205/r_{DA})$-

$$H_{DA}{}^s \cong H_{gc}H_{ec}\gamma/E_{av} \qquad (1a)$$

$$E_{av} = 2E_{gc}E_{ec}/(E_{gc} + E_{ec}) \qquad (1b)$$

$[\epsilon_{max}\Delta\nu_{1/2}h\nu_{max}]^{1/2}$, and the matrix elements can be evaluated from the DLCT absorption band.[1,7,19,28] This argument predicts that $h\nu_{max}$(IVCT) should decrease systematically with increasing α_{ec}, since $E_{ec} < E_{gc}$, so that $\Delta\epsilon_{ge} = (\epsilon_{ec} - \epsilon_{gc}) > 0$. The observed IVCT transition energies for the [M(MCL)(CN)$_2$]$^+$ and (4,4′-bpy)-bridged Ru(NH$_3$)$_5{}^{2+,3+}$ complexes do tend to decrease as $\Delta\epsilon_{ge}$ increases (Figure 3),[29] in reasonable accord with expectation, and the variations in $h\nu_{max}$(IVCT) can be taken as a measure of the coupling of the D/A system to BL. Since similar parameters appear in eq 1 and in $\Delta\epsilon_{ge}$, one expects that there should be a strong correlation between $\Delta h\nu_{max}$(IVCT) and $H_{DA}{}^s$ if superexchange coupling is important. This is consistent with the Sutton and Taube study but not with ours (Figure 1).

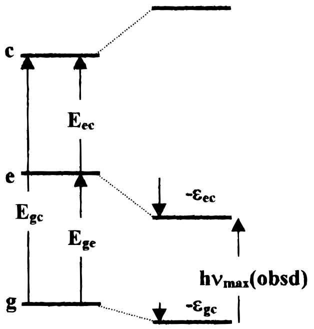

Figure 2. Schematic illustration of the three-state scheme used for the perturbation theory arguments in this paper.

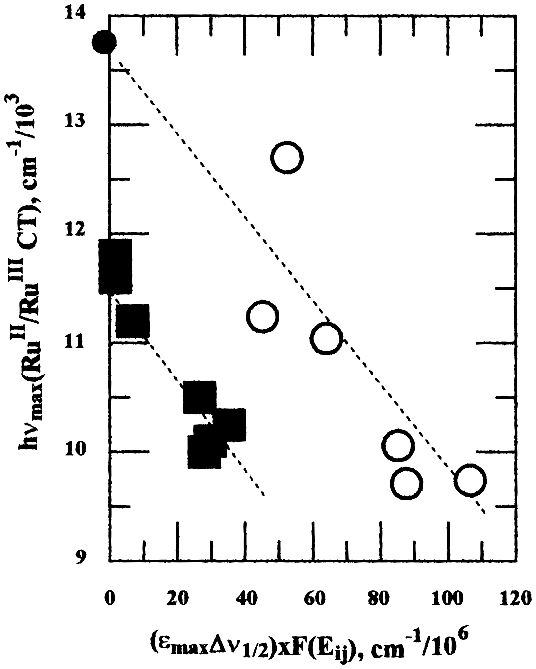

Figure 3. Perturbation-theory-based expectation for variations in $h\nu_{max}$(IVCT). It has been assumed that the two electron-transfer states are mixed only by means of coupling to the lowest energy metal to ligand CT (DLCT) excited state and that the mixing matrix elements are the same for both of these states ($H_{gc} = H_{ec}$). The solid circle is based on bimolecular electron self-exchange rate parameters (see text); the other points are as in Figure 1. $F(E_{ij}) = (E_{gc} - E_{ec})/E_{ec}$, ϵ_{max}, and $\Delta\nu_{1/2}$ are based on the DLCT and IVCT absorption band parameters.

That one of the standard spectroscopic signatures of the mixing between excited states (shifts of absorption maxima) is observed in the [M(MCL)(CN)$_2{}^+$]-bridged complexes while another (“intensity stealing” by the lower energy band) is not is consistent with symmetry-based vibronic Ru/M coupling in these complexes. The symmetry aspects are most easily formulated in the electron-transfer transition state for symmetric complexes in which the two electron-transfer states are degenerate, symmetric and antisymmetric combinations of the two valence-localized states. The perturbing {Ru(III),M(II),Ru(III)} CT excited state is electronically antisymmetric,[30,31] and only mixing with the antisymmetric electron-transfer state is electronically allowed. This constraint will be relaxed if the Ru(II)/M(III) mixing is promoted by coupling to the CN^- stretch,[17] since the symmetric (q_s, in phase) and antisymmetric (q_a, out of phase) combinations of CN^- stretches in the dicyano complexes will couple to mix the CT state with the electron-transfer states, leading to a secular equation of the form of eq 2[18] (where b_i is a linear vibronic constant appropriate to the mixing of the electron-transfer states with the DLCT state, b' is the linear vibronic constant appropriate for the mixing of the electron-transfer states, and V_c is the energy difference between the electron-transfer states and the CT state in the symmetry-adapted limit). The coupling of electronic states in the valence-localized situation can be approximately represented in a similar manner if the in- and out-of-phase matrix elements are represented as $H_{gc} = b_a q_a \cong b \cos\theta \approx b(1-\theta)$ and $H_{ec} = b_s q_s \cong b \sin\theta \approx b\theta$ for θ very small and assuming that $|b_i| \gg |b'|$.[32] For such a limit, $H_{DA}{}^s \approx 0$. The M-independent coupling that is observed in these complexes could arise from Ru/CN^- CT states.[17] The two CN^- centers (or the py centers of the 4,4′-bpy-like ligands of Taube's work) would give rise to symmetric and antisymmetric combinations of perturbing (MLCT) excited states, and the phase (or symmetry) issue would not be as clearly evidenced in the IVCT absorption intensity.

$$\begin{vmatrix} V_c - \epsilon & b_a q_a & b_s q_s \\ b_a q_a & -\epsilon & b' q_a \\ b_s q_s & b' q_a & -\epsilon \end{vmatrix} = 0 \qquad (2)$$

If the vibronic and solvational contributions are large enough to stabilize a charge-separated (or localized) ground state and taking $b' \approx 0$, the vertical energy difference between the electron transfer states, Δ_{ge}, will be given by eq 3, where δ_s is the contribution from the solvent. When $E_{ec} \cong (V_e - \Delta_{ge}) \le |H_{ec}|$, then $\psi_c \cong (\psi_e{}^o - \psi_c{}^o)/2^{1/2}$, $\psi_e \cong (\psi_e{}^o + \psi_c{}^o)/2^{1/2}$, and the phase (or symmetry) constraints should become less important. This is likely to be the case for the *trans*-$(py)_4Ru(CNRu(NH_3)_5)_2{}^{5+}$ complex[33,34] for which we find $\epsilon_{max}(IVCT) = 1700 \pm 200\ cm^{-1}\ M^{-1}$ and $h\nu_{max}(IVCT) = 10 \times 10^3\ cm^{-1}$.

$$\Delta_{ge} \cong [(b_a q_a)^2 + (b_s q_s)^2]/V + \delta_s \qquad (3)$$

While Figure 1 suggests that superexchange coupling ($H_{DA}{}^s$), mediated by BL, makes the major contribution to H_{DA} in the (4,4′-bpy)-bridged complexes, it also indicates that this contribution to H_{DA} is largely prohibited for the $[M(MCL)(CN)_2]$-bridged complexes. The IVCT transitions observed for $Ru(NH_3)_5{}^{3+,2+}$ couples bridged by $M(MCL)(CN)_2{}^+$ complexes appear to define an experimental limit in which D/A electronic coupling is not propagated down a chain of nearest-neighbor atoms and in which nuclear displacements of the atoms of the bridging ligand play a crucial role in determining $|H_{DA}|$. It seems likely that there are a variety of D/A coupling mechanisms, with the contributions of any one of them depending on the nature of the bridging ligand and the nature of the interactions between the D/A pair and the bridging ligand.

The synthesis and characterization of the $(MCL)M^{III}(CNRu(NH_3)_5)_2{}^{5+}$ [17] and $Ru(py)_4(CN)_2$[34] complexes have been described previously.

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References and Notes

(1) Newton, M. D. *Chem. Rev.* **1991**, *91*, 767.

(2) Barbara, P.; Meyer, T. J.; Ratner, M. *J. Phys. Chem.* **1996**, *100*, 13148.

(3) Reimers, J. R.; Hush, N. S. *Chem. Phys.* **1996**, *208*, 177.

(4) (a) Zhang, L.-T.; Ko, J.; Ondrechen, M. J. *J. Phys. Chem.* **1989**, *93*, 3030. (b) Zhang, L.-T.; Ko, J.; Ondrechen, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 1666. (c) Ferretti, A.; Lami. A.; Ondrechen, M. J.; Villani, G. *J. Phys. Chem. A* **1995**, *99*, 10484.

(5) Ferretti, A.; Lami, A.; Villani, G. *Inorg. Chem.* **1998**, *37*, 2779.

(6) Calzado, C. J.; Malrieu, J.-P.; Sanz, J. F. *J. Phys. Chem.* **1998**, *102*, 3659.

(7) (a) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005. (b) Hush, N. S. *Prog. Inorg. Chem.* **1967,** *9*, 391.

(8) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(9) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.

(10) Crutchley, R. J. *Adv. Inorg. Chem.* **1994**, *41*, 273.

(11) (a) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673. (b) Beratan, D. N.; Onuchic, J. N.; Betts, J. N.; Bowler, B. E.; Gray, H. B. *J. Am. Chem. Soc.* **1990**, *112*, 7915. (c) Jordan, K. D.; Padden-Row, M. N. *Chem. Rev.* **1992**, *92*, 395.

(12) McConell, H. M. *Chem. Phys.* **1961**, *35*, 508.

(13) Nelson, S. F.; Ismagilov, R. F.; Trieber, D. A., II *Science* **1997**, *278*, 846.

(14) Balzani, V.; Scandola, F. In *Comprehensive Supramolecular Chemistry*; Reinhart, D. N., Ed.; Pergamon: Oxford, 1996; Vol. 10, p 1.

(15) Debreczeny, M. P.; Svec, W. A.; Wasielewski, M. R. *Science* **1996,** *274*, 584.

(16) Gerfin, T.; Grätzel, M.; Walder, L. *Prog. Inorg. Chem.* **1997**, *44*, 345.

(17) (a) Watzky, M. A.; Endicott, J. F.; Song, X.; Lei, Y.; Macatangay, A. *Inorg. Chem.* **1996**, *35*, 3463. (b) Endicott, J. F.; Watzky, M. A.; Song, X.; Buranda, T. *Coord. Chem. Rev.* **1997**, *159*, 295. (c) Watzky, M. A.; Macatangay, A. V.; Van Camp, R. A.; Mazzetto, S. E.; Song, X.; Endicott, J. F.; Buranda, T. *J. Phys. Chem.* **1997**, *101*, 8441. (d) Endicott, J. F.; Song, X.; Watzky, M. A.; Buranda, T.; Lei, Y. *Chem. Phys.* **1993**, *176*, 427. (e) Macatangay, A. V.; Endicott, J. F. Work in progress.

(18) (a)Tsukerblat, B. S. *Group Theory in Chemistry and Spectroscopy*; Academic: London, 1994; Chapter 14, p 355. (b) Bersuker, I. B.; Borshch, S. A. *Adv. Chem. Phys.* **1992**, *LXXXI*, 703.

(19) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley-Interscience: New York; 1967.

(20) (a) Oh, D. H.; Boxer, S. G. *J. Am. Chem. Soc.* **1990**, *112*, 8161. (b) Oh, D. H.; Sano, M.; Boxer, S. G. *J. Am. Chem. Soc.* **1991,** *113*, 6880. (c) Shin, Y. K.; Brunschwig, B. S.; Creutz, C.; Sutin, N. *J. Phys. Chem.* **1996**, *100*, 8157. (d) Karki, L.; Lu, H. P.; Hupp, J. T. *J. Phys. Chem.* **1996**, *100*, 15637.

(21) Reimers, J. R.; Hush, N. S. *J. Phys. Chem.* **1991**, *95*, 9773.

(22) (a) Cave, R. J.; Newton, M. D. *Chem. Phys. Lett.* **1996**, *249*, 15. (b)Cave, R. J.; Newton, M. D.; Kumar, K.; Zimmet, M. D. *J. Phys. Chem.* **1995**, *99*, 17501.

(23) (a) Liang, C.; Newton, M. D. *J. Phys. Chem.* **1992**, *96*, 2855. (b) *J. Phys. Chem.* **1993**, *97*, 3199. (c) Curtiss, L. A.; Naleway, C. A.; Miller, J. R. *J. Phys. Chem.* **1995**, *99*, 1182.

(24) (a) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40. (b) Patqux, C.; Coudret, C.; Launay, J.-P.; Joachim, C.; Gourdon, A. *Inorg. Chem.* **1997**, *36*, 5037.

(25) (a) Saleh, A. A.; Crutchley R. J. *Inorg. Chem.* **1990**, *29*, 2132. (b) Evans, C. E. B.; Ducharme, D.; Naklicki, M. L.; Crutchley, R. J. *Inorg. Chem.* **1995**, *34*, 1350.

(26) (a) de la Rosa, R.; Chang, P. J.; Salaymeth, F.; Curtis, J. C. *Inorg. Chem.* **1985**, *24*, 4229. (b) Salaymeth, F.; Berhaue, S.; Yusof, R.; de la Rosa, R.; Fung, E. Y.; Matamoros, R.; Law, K. W.; Zheng, Q.; Kober, E. M.; Curtis, J. C. *Inorg. Chem.* **1993**, *32*, 3895.

(27) (a) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 4021. (b) Fischer, H.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 5512.

(28) Absorptivity ϵ_{max}, full-width at half-maximum $\Delta\nu_{1/2}$, the energy of the absorption maximum is $h\nu_{max}$, r_{DA} is given in angstroms, a Gaussian band shape, γ is a parameter which accounts for interlinker coupling[12] with energy units of cm^{-1}.

(29) The argument employed here is equivalent to setting $h\nu_{max}(IVCT) \cong \lambda_r + H.O.$ in the limit of no configurational mixing with higher energy electronic states, where the higher order (H.O.) contributions arise from differences in electronic repulsions (coulomb and exchange terms) and any shifts in the HOMO and LUMO energies which accompany the transition.[30] The intercept in Figure 3 is λ_r for the $Ru(NH_3)_5py^{2+,3+}$ couple based on a correlation of ion-pair charge-transfer absorption energy maxima with bimolecular (kinetic) self-exchange reorganizational parameters (adjusted

to $r_{DA} = 11.3$ Å). That the complexes bridged by the 4,4′-bipyridine class of ligands is consistent with this intercept is support for the simple treatment offered here. It should be noted that a recent theoretical treatment[5] of IVCT in this class of compounds appears to have neglected the solvent reorganizational contributions to $h\nu_{max}$(IVCT). Consequently, the estimate of $h\nu_{max} \approx 0.06$ eV in ref 5 may be a plausible estimate of the H.O. contributions.

(30) (a) Lever, A. B. P.; Dodsworth, E. S. In *Inorganic Electronic Structure and Spectroscopy*; Lever, A. B. P., Solomon, E. I., Eds.; Wiley: New York, in press; Vol. II, Chapter 1. (b) Gorelsky, S. I.; Kotov, V. Yu.; Lever, A. B. P. Submitted for publication.

(31) The details of the electronic symmetry of these trimetallic complexes can be complicated.[17c] The simplified argument employed is analogous to three-center bonding arguments.

(32) In terms of the correlated nuclear displacements, $\theta = 2\pi x/a$, where x is the instantaneous and a is the maximum displacement of the coupled oscillator. The phase difference of the matrix elements of eq 2 corresponds to a phase difference of the mixing coefficients, (H_{gc}/E_{gc}) and (H_{ec}/E_{ec}) in a perturbation theory formalism. The phase differences would not affect the energies, which depend on $\langle \psi_i | H | \psi_i \rangle^2$, while there would be some cancellation of the perturbational effects in the intensity that depends on $\langle \psi_e | H | \psi_g \rangle^2$.

(33) The $Ru(py)_4{}^{2+}/Ru(NH_3)_5{}^{3+}$ CT absorption maximum ($h\nu_{max} \approx 12 \times 10^3$ cm^{-1} [34]) is near that for the IV transition in relatively "unperturbed" ion pairs and $H_{ec} \approx 3 \times 10^3$ cm^{-1}.[17e] The width of the IVCT transition in the $Ru(py)_4(CN)_2$-bridged complex is about 5×10^3 cm^{-1}, similar to that of the other dicyanometalate-bridged complexes. In the limit discussed here, the distinction between MLCT and IVCT transitions is not meaningful. However, this distinction is still useful when $\lambda_r \gg \Delta G_s$ and $E_{ec} > |H_{ec}|$.

(34) Coe, B. J.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1995**, *34*, 3600.

(35) Values of ϵ_{max} were estimated from initial and final slopes of plots of absorbance change vs [Fe^{3+}] added.[17] For dipyridyl bridges in Figure 1: b1 = 4,4′-dipyrdylmethane; b2 = bis(4-pyrdyl)sulfide; b3 = 3,3′-dimethyl-4,4′-dipyridyl; b4 = 4,4′-dipyridylacetylene; b5 = 4,4′-dipyridylethylene; b6 = 4,4′dipyridyl. MCL ligands of the *cis*(*c*)- and *trans*(*t*)-$M(MCL)(CN)_2{}^+$ bridges: t1 = 1,4,8,11-tetraazacyclotetradecane; t2 = 5,12-*ms*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; t3 = 1,4,8,12-tertaazacyclopentadecane; c1 = 1,4,8,11-tetraazacyclotetradecane; c2 = 5,12-*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.