The aspects of the successive –up–down–up–down– orientation of the ligand bisector relative to the polymer axis in both structures suggests interleaving of the aromatic ring planes from successive strands up *b* (cf. ref 6). The increased successive Pb···Pb separation on passing from **1** to **2** is accompanied by increased twist of the ligand about its 2-fold axis so that it is more sharply inclined to the polymer axis, enabling interplanar spacings to remain substantially constant at typical charge-transfer distances. It is of interest that, while successive "up-down" lead atoms in **2** are bridged in an eight-membered ring (note that the thiocyanate ligands are substantially parallel to the terpy in the projections of Figure 2, with bridges to neighboring lead atoms by Pb–S–C angles of 94.6 (4)°), in **1**, successive lead atoms are bridged at the shorter distance by PbS_2Pb four-membered rings, while the other bridging functionality of the sulfur enables a leap to the subsequent lead atom of similar disposition: Pb(up)–S–C–N–Pb(up). The subtlety of factors influencing thiocyanate coordination modes is well-known[7] and well-illustrated by the present and related[8] studies.

Acknowledgment. We gratefully acknowledge partial support of this work by a grant from the Australian Research Grant Scheme.

Supplementary Material Available: Tables Sup-1–Sup-7, listing crystal and refinement data, thermal parameters, derived hydrogen atom parameters, and phenanthroline and terpyridyl geometries (6 pages); tables of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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Resonance Raman Spectra and Electrochemistry of Mononuclear and Dinuclear (Bis(pyridinyl)triazolato)ruthenium Compounds

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Recently, the synthesis and properties of mononuclear and dinuclear $Ru(bpy)_2$ compounds containing bpt have been reported[2a] (bpy = 2,2′-bipyridine; Hbpt = 3,5-bis(pyridin-2-yl)-1,2,4-triazole; see Figure 1). The bpt anion in the mononuclear compound is coordinated via N1 of the triazole ring and a pyridine ring to the ruthenium ion; in $[(Ru(bpy)_2)_2(bpt)]^{3+}$, the second $Ru(bpy)_2$ moiety is bound via N4 of the triazole ring and the second pyridine ring.[2a,b] The properties of the dinuclear system are unusual since a rather extensive electron delocalization in the mixed-valence system has been observed. Furthermore, the dinuclear compound emits at room temperature.[2a] Resonance Raman (rR) spectroscopy has often been used to investigate the origin of electronic absorption bands.[3] With the use of this technique, extensive information concerning the electronic structures of various compounds has been obtained.[3] If the observed MLCT (metal to ligand charge transfer) band is due to both Ru → π^*(bpy) and Ru → π^*(bpt) transitions, then a distinct wavelength dependence in the rR spectra should be manifested within the range of the observed transition. On the other hand, if the absorption band would be caused only by Ru → π^*(bpy) transitions, then in all cases the same rR spectra should be observed.

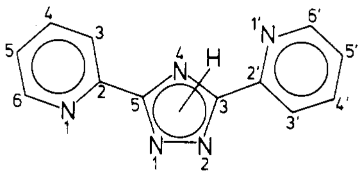

Figure 1. Structural formula of 3,5-bis(pyridin-2-yl)-1,2,4-triazole (Hbpt).

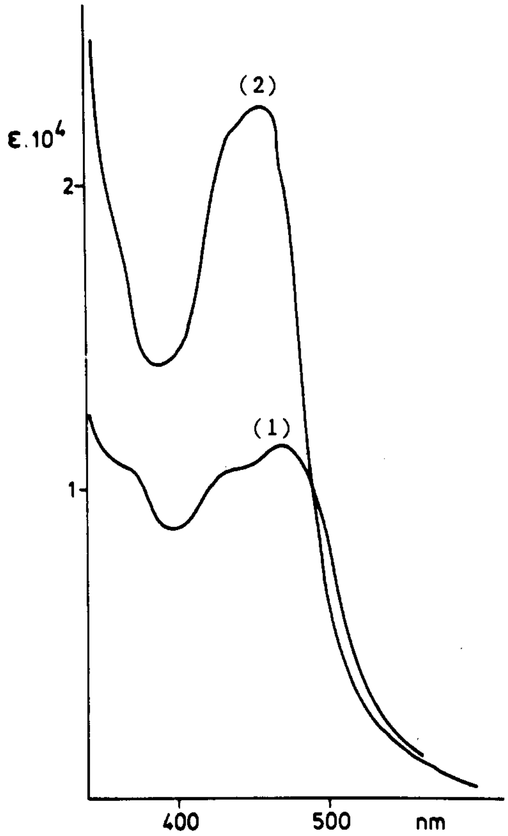

Figure 2. Absorption spectra of $[Ru(bpy)_2(bpt)]^+$ (cation of **1**) and $[(Ru(bpy)_2)_2(bpt)]^{3+}$ (cation of **2**). All compounds were measured in ethanol with a concentration of about 10^{-4} mol/L.

Pyrazoles, imidazoles, and triazoles are known to have high-lying π^* orbitals.[4,5] It is therefore of interest to study whether

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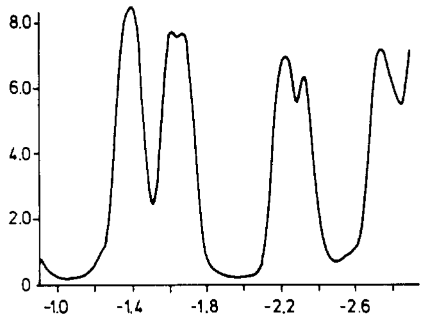

Figure 3. Differential-pulse polarogram of $[(Ru(bpy)_2)_2(bpt)]^{3+}$ (cation of **2**). The measurement has been carried out in acetonitrile with 0.1 M TBAP.

Table I. MLCT Bands and Reduction Potentials of the Mononuclear and Dinuclear Compounds with bpt

	abs band,[a] nm	redn potentials,[b] V
$[Bu(bpy)_2(bpt)]PF_6$ (**1**)	475 (1.13)	−1.47, −1.73, −2.27, −2.45, −2.55
$[(Ru(bpy)_2)_2(bpt)](PF_6)_3$ (**2**)	452 (2.26)	−1.40, −1.62, −1.67, −2.23, −2.33, −2.74

[a] Measured in ethanol; values in parentheses are extinction coefficients × 10^4. [b] Measured by using differential-pulse polarography in acetonitrile with 0.1 M tetraethylammonium perchlorate (TEAP). All values are versus SCE.

excitation to the π^* orbital of the dinucleating bpt ligand gives rise to a part of the MLCT band. If the bpt π^* orbital is populated, this can have important consequences for the nature of the emitting excited state.

In this note, the MLCT bands have been assigned by using rR spectroscopy and electrochemical measurements. With the use of these techniques, detailed information concerning the electronic structure of these compounds has been obtained.

Experimental Section

$[Ru(bpy)_2(bpt)]PF_6$ (**1**) and $[(Ru(bpy)_2)_2(bpt)](PF_6)_3$ (**2**) have been prepared as described previously.[2a] Purity has been checked by using NMR spectroscopy and elemental analysis.[2a] The rR spectra were recorded in CH_3CN solution by using a spinning cell and a Jobin Yvon HG2S Ramanor. The samples were excited by an SP Model 171 argon ion laser. Laser power was 50–100 mW and spectral slit width was 10 cm^{-1}. Excitation took place at 458, 488, and 514.5 nm. Electrochemical measurements have been carried out by using an EG&G Par C Model 303 with an EG&G 384B polarographic analyzer. The differential-pulse polarograms of the reduction potentials have been obtained at a scan rate of 4 mV/s with a pulse height of 20 mV.

Results and Discussion

The absorption spectra of $[Ru(bpy)_2(bpt)]^+$ (cation of **1**) and $[(Ru(bpy)_2)_2(bpt)]^{3+}$ (cation of **2**) are presented in Figure 2. Both compounds show MLCT bands around 450 nm, which is at an energy comparable to that of the Ru(II) → π^* transitions in $[Ru(bpy)_3]^{2+}$.[3a]

The differential-pulse polarogram of the dinuclear compound is shown in Figure 3. The reduction potentials and the energies of the MLCT bands are listed in Table I.

Because of the similarities of the reduction potentials of these compounds to those found for $[Ru(bpy)_3]^{2+}$, the peaks at about −1.40 and −1.72 V vs SCE have been assigned to the bpy-based reductions.[4]

The reduction of the bpt ligand is observed at a much more negative potential, and most probably the peaks at −2.23 and −2.33 V vs SCE can be explained by bpt-based reductions.

The rR spectra of the mononuclear compound (excitation at 458 and 514.5 nm, respectively) are presented in Figure 4. The vibrations of the bpy ligands are clearly observable at 1600, 1554, 1485, 1315, 1268, 1168, 1024, and 644 cm^{-1}. These assignments are based on a comparison with literature data of other $Ru(bpy)_x$ compounds.[3] Excitation at 488 nm yielded the same rR spectrum, and again, no bpt vibrations were resonance enhanced. Unfortunately, no rR spectra could be obtained with exciting laser lines having λ > 514.5 nm, because of disturbing luminescence. Similar results were obtained for the dinuclear compound, only vibrations of bpy being observed.

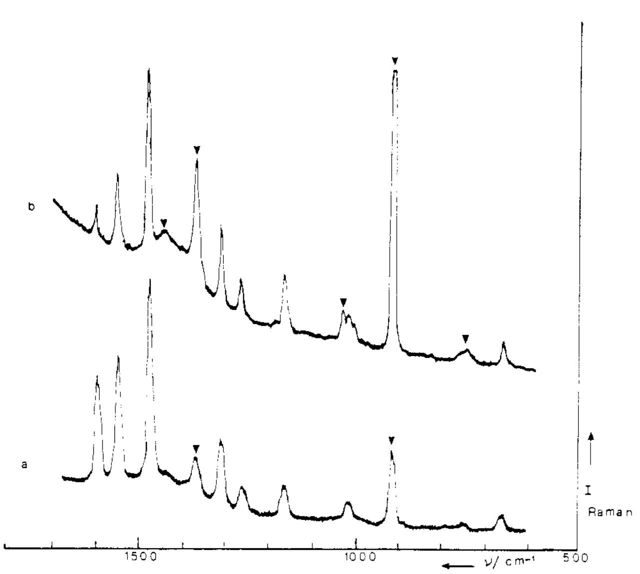

Figure 4. Resonance Raman spectrum of $[Ru(bpy)_2(bpt)]PF_6$ (**1**) in acetonitrile, obtained by excitation with λ = 458 nm (a) and λ = 514.5 nm (b). Bands indicated with a v are solvent bands.

These results clearly confirm the data obtained from the electrochemical measurements: the lowest energy MLCT band of compounds **1** and **2** can be explained by Ru → π^*(bpy) MLCT transitions. No transitions to π^*(bpt) orbitals are observed in this part of the absorption spectra.

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Preparation, Molecular Structure, and Magnetism of $[LFe(\mu\text{-}O)(\mu\text{-}CO_3)_2FeL]\cdot 4.25H_2O$ (L = 1,4,7-Trimethyl-1,4,7-triazacyclononane)

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The metalloprotein lactoferrin is known to reversibly bind two iron(III) ions concomitantly with two CO_3^{2-} (or HCO_3^-) groups.[2] A synergistic relationship between cation and anion binding has been established.[3] The determination of the crystal structure of human lactoferrin at 3.2-Å resolution[4] established that two oc-

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