

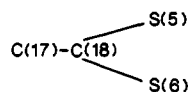
Table III. Bond Distances (Å) and Angles (deg) in Complex II

Bi-S(1)	3.108 (2)	B-S(5)	2.963 (2)
Bi-S(2)	2.647 (1)	Bi-S(3)	3.040 (1)
Bi-S(6)	2.617 (2)	Bi-S(4)	2.626 (1)
S(2)-C(1)	1.770 (6)	S(1)-C(1)	1.701 (5)
S(4)-C(9)	1.763 (6)	S(3)-C(9)	1.712 (5)
S(6)-C(17)	1.764 (6)	S(5)-C(17)	1.717 (7)
N(1)-C(7)	1.470 (8)	N(1)-C(6)	1.325 (6)
N(2)-C(15)	1.478 (8)	N(2)-C(14)	1.331 (7)
N(3)-C(23)	1.471 (8)	N(3)-C(22)	1.323 (10)
C(2)-C(3)	1.514 (7)	C(1)-C(2)	1.394 (7)
C(3)-C(4)	1.536 (8)	C(2)-C(6)	1.417 (8)
C(5)-C(4)	1.526 (8)	C(5)-C(6)	1.495 (7)
C(9)-C(10)	1.394 (8)	C(7)-C(8)	1.534 (10)
C(10)-C(14)	1.409 (8)	C(10)-C(11)	1.514 (7)
C(12)-C(13)	1.517 (8)	C(11)-C(12)	1.540 (9)
C(15)-C(16)	1.518 (8)	C(13)-C(14)	1.506 (8)
C(18)-C(19)	1.523 (11)	C(17)-C(18)	1.381 (9)
C(19)-C(20)	1.544 (10)	C(18)-C(22)	1.422 (9)
C(21)-C(22)	1.511 (10)	C(20)-C(21)	1.534 (11)
		C(23)-C(24)	1.518 (12)
S(1)-Bi-S(2)	61.9 (4)	S(5)-Bi-S(6)	53.7 (3)
S(1)-Bi-S(3)	129.8 (5)	S(1)-Bi-S(5)	127.6 (4)
S(3)-Bi-S(4)	63.0 (5)	S(3)-Bi-S(5)	86.8 (4)
S(2)-Bi-S(4)	79.4 (5)	S(2)-Bi-S(6)	83.6 (3)
S(4)-Bi-S(6)	93.0 (4)	Bi-S(2)-C(1)	96.5 (2)
Bi-S(4)-C(9)	94.6 (2)	Bi-S(6)-C(17)	94.2 (2)
C(6)-N(1)-C(7)	123.0 (5)	C(14)-N(2)-C(15)	123.3 (5)
C(22)-N(3)-C(23)	122.6 (6)	S(1)-C(1)-S(2)	118.8 (3)
S(1)-C(1)-C(2)	126.5 (4)	S(2)-C(1)-C(2)	114.7 (4)
C(1)-C(2)-C(3)	123.6 (5)	C(1)-C(2)-C(6)	126.7 (4)
C(3)-C(2)-C(6)	109.6 (4)	C(2)-C(3)-C(4)	105.4 (5)
C(6)-C(5)-C(4)	105.6 (5)	N(1)-C(6)-C(2)	125.5 (5)
N(1)-C(6)-C(5)	123.4 (5)	C(2)-C(6)-C(5)	111.1 (4)
N(1)-C(7)-C(8)	113.4 (6)	S(3)-C(9)-S(4)	118.2 (3)
S(3)-C(9)-C(10)	125.7 (4)	S(4)-C(9)-C(10)	116.1 (4)
C(9)-C(10)-C(11)	124.0 (5)	C(9)-C(10)-C(14)	127.0 (5)
C(11)-C(10)-C(14)	108.9 (5)	C(10)-C(11)-C(12)	103.7 (4)
C(11)-C(12)-C(13)	106.2 (5)	C(12)-C(13)-C(14)	103.7 (5)
N(2)-C(14)-C(10)	125.8 (5)	N(2)-C(14)-C(13)	123.0 (5)
C(10)-C(14)-C(13)	111.1 (5)	N(2)-C(15)-C(16)	112.1 (5)
S(5)-C(17)-S(6)	116.3 (3)	S(5)-C(17)-C(18)	127.0 (5)
S(6)-C(17)-C(18)	116.7 (5)	C(17)-C(18)-C(19)	125.5 (6)
C(17)-C(18)-C(22)	125.3 (7)	C(19)-C(18)-C(22)	109.1 (6)
C(18)-C(19)-C(20)	104.0 (6)	C(19)-C(20)-C(21)	105.8 (6)
C(20)-C(21)-C(22)	104.2 (5)	N(3)-C(22)-C(18)	126.0 (6)
N(3)-C(22)-C(21)	123.2 (6)	C(18)-C(22)-C(21)	110.7 (6)
N(3)-C(23)-C(24)	107.7 (6)	C(3)-C(4)-C(5)	107.1 (4)

oms.^{10a} Neutral atom scattering factors were those of Cramer and Weber.^{10b} Final atomic parameters are listed in Table II and a view of the structure is given in Figure 1. Lists of observed and calculated structure factors, anisotropic thermal parameters, and H atom coordinates are available.⁵

Results and Discussion

The Bi(H₁EACDA)₃ complex can be prepared by treatment of either a solution of BiCl₃ or a suspension of BiOCl in ethanol with EACDA. The structure exhibits discrete neutral Bi(C₈H₁₂NS₂)₃ species with S₆ ligand donor sets. The N atom is not coordinated to the Bi(III) ion as it is at least 5.808 Å away. Each of the C-CS₂ units is planar to within ±0.004 Å. The plane described by

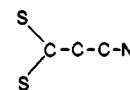


(third ligand; Figure 1) makes an angle of 74.6° with the plane described by the same unit of the first ligand and an angle of 86.0° with the plane described by the second ligand. Thus, the coordination geometry around Bi(III) can be described as trigonal antiprismatic. Only one other structure of a Bi(III) 1,1-dithio complex, tris(diethyldithiocarbamate)bismuth(III) (Bi(Et₂Dtc)₃,

has been reported and a similar coordination geometry is present in that complex.⁶

As also seen in the tris(diethyldithiocarbamate) complex, bismuth is coordinated asymmetrically by each dithio ligands in such a way that there are three short Bi-S bonds [Bi-S(2), 2.647 (1) Å; Bi-S(4), 2.626 (1) Å; Bi-S(6), 2.617 (2) Å] and three long Bi-S bonds [Bi-S(1), 3.108 (2) Å; Bi-S(3), 3.040 (5) Å; Bi-S(5), 2.963 (5) Å]. Thus, S(1), S(3), and S(5) and likewise S(2), S(4), and S(6) form triangular faces in the coordination polyhedron. The molecular symmetry around Bi(III) is closer to C₃. The asymmetric binding of the dithio ligands may be attributed to the presence of a stereochemically active lone pair on the Bi(III) ion. If the lone pair lies along the 3-fold axis, the S(1), S(3), and S(5) atoms on the same side as the lone pair are pushed away from the Bi(III) ion, resulting in longer Bi-S bond lengths.

The S-C-S bond angles, which range from 116.3 (3) to 118.8 (3)°, are also similar to those found in the diethyldithiocarbamate complex of Bi(III).^{6,7} In contrast, when 1,1-dithio ligands are bound to metal ions in a symmetrical fashion (both M-S bonds equal in length), the S-C-S angles are shorter⁷ (110 (1) to 113 (1)°), signifying greater strain at the sp² C atom. S-Bi-S bond angles are within 61.6-63.7° as found in other Bi(III) complexes.^{6,11} The C-C bond lengths between the C atom of the CS₂ group and the one bonded to it lie between 1.394 (7) and 1.381 (9) Å, showing appreciable double bond character. The



group is slightly distorted from planarity (within ±0.014 Å). The S(1) atom from the nearest neighbour is 3.689 Å away from the Bi(III) ion of the original molecule, signifying a weakly bonded dimeric structure. This distance in this EACDA complex is much longer than the 3.389 Å distance found in the related diethyldithiocarbamate complex.

Further studies of complexes formed by derivatives of the H₁EACDA ligand are in progress.

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Supplementary Material Available: Listings of anisotropic thermal parameters and hydrogen atom coordinates (2 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

(11) Bharadwaj, P. K. and Musker, W. K., to be submitted for publication.

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Time-Resolved Resonance Raman Spectra of Polypyridyl Complexes of Ruthenium(II)

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Time-resolved resonance Raman (TR³) spectroscopy has recently evolved as a powerful tool for the investigation of the dynamics and structures of a variety of reactive intermediates, electronic excited states, biological systems, and enzyme-substrate

(10) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) pp 149-159; (b) pp 99-101.

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Chart I. Structures of I-III

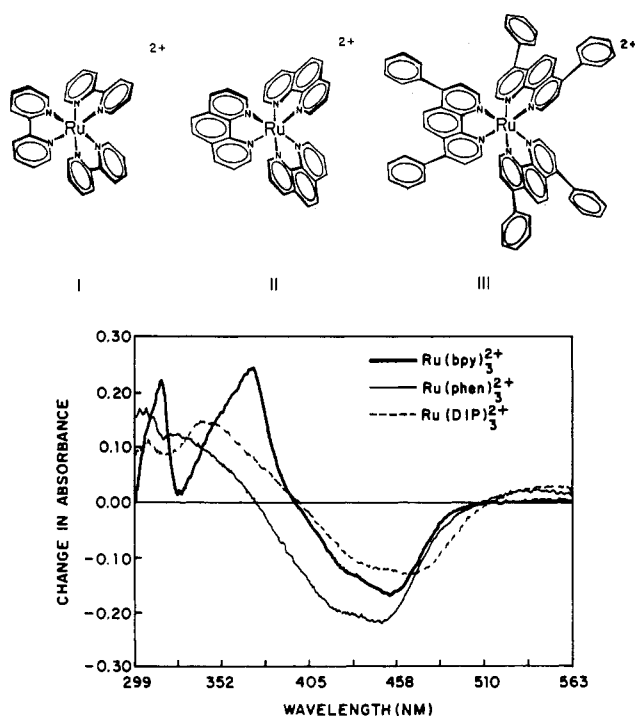


Figure 1. Absorption spectra of I-III upon excitation at 354.5 nm, 10 ns after excitation.

complexes.^{1,2} In this communication, we report the TR³ spectra of three ruthenium complexes of special importance because of their binding ability to nucleic acids, because of their success as chiral probes that recognize the conformations and helicity of nucleic acids, and because of their potential to serve as models for the interaction of metal ions with nucleic acids.³

It has been shown first by Woodruff⁴ and later by others⁵ that the TR³ spectrum of the lowest excited electronic state of Ru(bpy)₃²⁺ possesses strong similarities to that of the radical anion of the ligand, i.e., bpy^{•-}. Electrochemical reduction of Ru(II) complexes leads to charge localization in the ligands.⁶ Hence,

- (1) (a) Atkinson, G. H. *Time-Resolved Raman Spectroscopy*; Eds. Clark, R. J. H., Hester, R. E., Eds.; Heyden: London, 1982; Vol. 9, p 1. (b) El-Sayed, M. A. *Pure Appl. Chem.* **1986**, *57*, 187. (c) Terner, J.; El-Sayed, M. A. *Acc. Chem. Res.* **1985**, *18*, 331. (d) Johnson, C. K.; Dalickas, G. A.; Payne, S. A.; Hochstrasser, R. M. *Pure Appl. Chem.* **1985**, *57*, 195. (e) Hayward, G.; Carlsen, W.; Siegman, A.; Stryer, L. In *Picosecond Phenomena II*; Hochstrasser, R. M., Kaiser, K., Shank, C. V., Eds.; Springer Series in Chemical Physics 14; Springer-Verlag: West Berlin, 1980; p 377. (f) Rossetti, R.; Brus, L. E. *J. Am. Chem. Soc.* **1984**, *106*, 4336.
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- (3) (a) Barton, J. K. *Comments Inorg. Chem.* **1985**, *3*, 321. (b) Kumar, C. V.; Barton, J. K.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 708. (c) Barton, J. K.; Goldberg, J. M.; Kumar, C. V.; Turro, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 2081. (d) Barton, J. K.; Basile, L. A.; Danishefsky, A.; Alexandrescu, A. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 1961. (e) Barton, J. K.; Danishefsky, A. T.; Goldberg, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2172. (f) Kumar, C. V.; Raphael, A. L.; Barton, J. K. *Biomolecular Stereodynamics*; Adenine: Schenectady, NY, 1985; Vol. III, p 87.
- (4) (a) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391. (b) Bradly, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441. (c) Woodruff, W. H. In *Inorganic Chemistry: Toward the 21st Century*; Chisholm, M. H., Ed.; ACS Symposium Series 211; American Chemical Society: Washington, DC, 1983. (d) Woodruff, W. H.; Dallinger, R. F.; Hoffman, M. Z.; Bradly, P. G.; Presser, D.; Malvey, V.; Kessler, R. J.; Norton, K. A. In *Time-Resolved Vibrational Spectroscopy*; Atkinson, G. H., Ed.; Academic: New York, 1983.
- (5) (a) Smother, W. K.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1067. (b) Mabrouk, P. A.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 526. (c) Forster, M.; Hester, R. E. *Chem. Phys. Lett.* **1981**, *81*, 42.

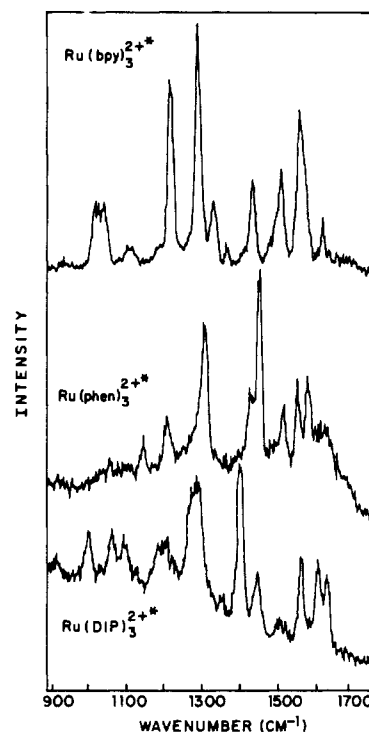


Figure 2. TR³ spectra of Ru(II) complexes upon excitation at 354.5 nm. The excited states of these complexes have significant absorption at this wavelength, hence the same laser pulse can serve as both pump and probe pulses.

Table I. Resonance Raman Frequencies (cm⁻¹) of I-III under Pulsed Excitation (354.5 nm)^a and Steady-State Excitation (441.6 nm)^b

Ru(bpy) ₃ ²⁺		Ru(phen) ₃ ²⁺		Ru(DIP) ₃ ²⁺	
354.5 nm	441.6 nm	354.5 nm	441.6 nm	354.5 nm	441.6 nm
1015	1028			996	889
1100	1174	1149	1145		1264
1289			1291		1288
1323	1317	1312			
		1435		1404	
1427	1489	1460	1451	1449	1440
1503		1524	1515		
1553	1560	1557	1579	1560	1556
		1584			
1611	1604			1603	1594
			1629	1626	

^a The excited state TR³ spectra were recorded by excitation with a single pulse at 354.5 nm employing an Nd:YAG laser (15 mJ, ca 8 ns, 20 Hz) by focusing on to a jet stream of the sample solution (0.2–0.3 mM) in water. The low solubility of III required the use of 500 mM SDS to achieve a convenient level of solubility. The spectra shown are adjusted for background subtraction. The Raman scattered light was collected and dispersed by using a Spex triple-mate monochromator and was focused on to a cooled PMT (RCA C31034a). The signals were analyzed by using a PARC 4400 boxcar apparatus. In some experiments the PMT was replaced by a PARC OMA III detector, interfaced with a PDP-11 computer. ^b The ground-state spectra were obtained by excitation with a Liconix He-Cd laser (441.6 nm, 40 mW; 325 nm, 10 mW) with the same experimental setup for the TR³ spectra, employing an OMA III detector and electronics.

it has been concluded that the excited state can be described as a metal-to-ligand charge-transfer state (MLCT) in which the excited electron is localized on one of the ligands during the time scale of the TR³ experiment.⁷ We report here the results of TR³

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- (7) Solvent reorganization and vibronic coupling have been suggested as two of the main reasons for charge localization. See: (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (b) Hush, N. S. *Chem. Phys.* **1975**, *10*, 361. (c) Launay, J. P.; Babonneau, F. *Chem. Phys.* **1982**, *67*, 295.

and transient absorption experiments which demonstrate that the excited states of three Ru(II) complexes, (Chart 1) tris(2,2'-bipyridyl)ruthenium(II) dichloride (I), tris(1,10-phenanthroline)ruthenium(II) dichloride (II), and tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) dichloride (III), are indeed localized on the ligand.

Presented in Figure 1 are the excited-state absorption spectra for I-III recorded 10 ns after Nd:YAG laser excitation at 354.5 nm, uncorrected for the ground-state absorption.⁸ The transient excited-state absorption spectrum of I is considerably red shifted compared to those of II and III. These difference spectra clearly show that the excited state of I absorbs more at 354.5 nm than those of II and III. The ground states of all of the complexes possess very little absorbance at 354.5 nm. As a result, the excited states of II and III should show less resonance enhancements at this wavelength than that of I. This is probably a contributing factor to the absence of reports of the TR³ spectrum of II in the literature. The excited-state resonance Raman spectra of II and III, along with that of I, are shown in Figure 2.

With sodium sulfate (0.5 M) used as an internal standard, the Raman intensities of I and II were compared and the lines in the spectrum of II were found to be at least 5-6 times weaker than that those in the spectrum of I. Increasing the pulse energies up to 40 mJ did not produce significant differences in the spectra, consistent with saturation of excited-state population, under pulsed excitation conditions. For comparison, the ground-state resonance Raman (RR) spectra of these complexes were measured,⁹ and these frequencies are listed in Table I.

The TR³ spectra of I-III are quite distinct from the corresponding ground-state spectra. Thus, all the available evidence is consistent with the assignment of the TR³ spectra shown in Figure 2 to the triplet electronically excited states of I-III. The TR³ spectrum of II is considerably different from the ground-state spectrum of II obtained by 441.6-nm excitation (or 325-nm excitation). The ground-state spectrum obtained at 350.7 nm is also different from the excited-state spectrum.⁹ The differences in the TR³ spectra of I-III are attributed to electron localization on different ligands associated with the metal center.¹⁰

In conclusion, the TR³ spectra of II and III have been obtained for the first time. The excited-state spectrum of II is extremely weak, which is at least in part due to the low extinction coefficient for the excited state at 354.5 nm (Figure 1). On the basis of earlier assignments of the TR³ spectra of ruthenium complexes^{4,5} we suggest that these states are also ligand-localized MLCT states. The striking dissimilarities among the spectra of I-III, open the possibility of investigation of the electronic nature of the excited states of the mixed chelates of Ru(II) containing these ligands, of probing the relative distributions of the excited-state electron on different ligands, and of the study of electron hopping from ligand to ligand within the same complex. The results of these investigations will be reported shortly.

Acknowledgment. The authors thank Drs. M. B. Zimmt and M. Paczkowski for their outstanding assistance in the design and construction of the Raman spectrometer. For helpful discussions and for copies of the 350.7-nm excitation Raman spectra of II, Dr. W. H. Woodruff (Los Alamos) is gratefully acknowledged. We also thank the National Science Foundation and the Army Research Office for their generous support of this work.

- (8) The samples were excited perpendicular to the monitoring light beam. The spectra with and without laser excitation were collected after dispersion through an ISA HR-320 spectrograph and PARC OMA-111 detector. The spectrograph was calibrated with mercury emission lines.
- (9) For some of the ground-state RR spectra see: Bradley, P. G. Ph.D. Thesis, The University of Texas at Austin, 1982. Basu, A.; Gafney, H. D.; Streckas, T. C. *Inorg. Chem.* **1982**, *21*, 2231. For excited-state spectral correlations, see: McClanahan, S. F.; Dallinger, R. F.; Hoiler, F. J.; Kincaid, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 4853.
- (10) We were unable to obtain the resonance Raman spectrum of the phen radical ion due to its instability under our experimental conditions. To the best of our knowledge, the resonance Raman spectrum of this species has not been reported in the literature. If our assignment of the TR³ spectrum of II is correct, then the spectrum shown in Figure 2 can serve as a basis for construction of the resonance Raman spectrum of II.

Registry No. Ru(bpy)₃²⁺, 15158-62-0; Ru(phen)₃²⁺, 22873-66-1; Ru(DIP)₃²⁺, 63373-04-6.

Supplementary Material Available: Figure 3, ground-state resonance Raman spectra of I-III (1 page). Ordering information is given on any current masthead page.

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X-ray Structural Characterization and Magnetic Properties of a Novel Tetranuclear Copper Catecholate

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The interaction of catechols with transition-metal ions has attracted much recent interest¹ due to its biological relevance as well as its possible involvement in synthetic procedures. Several copper complexes of catechols²⁻⁹ and semiquinones⁹⁻¹¹ have been studied in this context; however, structural characterizations of these kinds of compounds have only appeared in the very recent past,^{7,9,11} and in all but one case,⁷ chelating catechols or semiquinones were observed. As part of a project aimed at synthesizing multinuclear complexes of redox-active ligands, we investigated the possibility of binding catechols in a new unsymmetrical (nonchelating) mode in order to use the other (or both) oxygen(s) to complex a second metal ion. In this report we describe the structural and magnetic properties of a tetranuclear copper bis-(catecholato) complex in which each catecholate is bound to three copper atoms of a tetranuclear cluster and exhibits both the chelating and two different bridging bonding modes.

The catechol ligands (H₂L) are prepared by condensation of 2,3-dihydroxybenzaldehyde with the corresponding (amino-alkyl)pyridine as unstable off-white solids. The various complexes are obtained upon reacting an ethanol solution of the ligand with the chosen copper salt and recrystallizing the resulting green (or brown in the case of the acetates) powder from methanol. The X-ray structure of [Cu₂(L₂)(CH₃CO₂)₂]₂·H₂O (**4**) was determined on pale brown crystals that formed upon slow evaporation of a methanol solution.¹²

The structure of the complex is shown in Figure 1.^{13,14} The molecule is composed of two halves related by a center of symmetry located at the center of the Cu₂O1Cu₂O1' parallelogram. Each half of the molecule is constituted by a dicopper unit where the metal atoms are bridged by the ligand and two acetate ions. The symmetry around Cu1 is close to a trigonal bipyramid with the pyridine nitrogen N2 and the bridging oxygen O2 from the catechol occupying the axial positions of the bipyramid. On the other hand, the environment of Cu2 approaches a square pyramid whose basal plane comprises an acetate oxygen O4 and three oxygens from the catechols, and the apical position is occupied by a fifth oxygen, O6, from a different acetate. The Cu1...Cu2 distance within this dinuclear moiety is 3.303 Å. This distance is longer than the Cu2...Cu2' distance (3.053 Å) observed between the two dinuclear units. The reason for this lies in the fact that in the latter case only one-atom bridges are involved while two three-atom bridges (acetate) are present in the former. Finally, it is to be noted that mean C-O and C-C bond lengths are 1.33 and 1.41 Å, respectively, which supports the copper(II)-catecholate formulation.^{1,9}

The bonding mode exhibited by the catecholate in the dinuclear units of **4** is exactly the one proposed to occur in an intermediate

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