sorption spectra show one main progression in a ν_δ' normal mode, which means that the only strong force exerted in the excited-state conformations ^1B_g (trihydrate) and ^1A (monohydrate) is along the Q_δ coordinate. This results in a motion outward of the propanediamine ligands along the $x + y$ molecular axes, which is realistic since the lowest energy transition involves promotion to an antibonding $d_{x^2-y^2}$ orbital, which has four lobes pointing along the x and y molecular axes containing the N atoms. Therefore, the force (eq 3) will have an appreciable amplitude along such normal coordinates Q, for which the gradient $\partial H/\partial Q = \partial V/\partial Q$ of the dynamic ligand field exhibits the same directional property. This condition is best fulfilled by the ν_δ mode, because of the sizable contribution of Co–N bond stretching coefficients to this mode.

Apart from the Q_δ mode, there are further normal modes of vibrations that involve comparable amounts of Co–N bond stretching and that therefore might have the same significance as Q_δ. However, in comparison with the latter, these normal modes involve larger contributions of Co–C, C–N and C–C stretching coordinates and therefore exhibit greater force constants. These greater force constants lead to greater resistance to distortion, and hence the corresponding displacements become small and are not measurable. This means that even if those modes are mixed with the ν_δ mode, resulting in rotation of their normal coordinates in the excited state relative to the normal modes in the ground state (i.e., the Dushinsky effect[5,14]), they contribute only negligibly to the absorption band.

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Supplementary Material Available: Listings of final atomic fractional coordinates, thermal parameters, and interatomic distances and angles (3 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Coordination Behavior of N-Protected Aspartic Acid in Binary and Ternary Copper(II) Complexes. Crystal and Molecular Structure of Bis(2,2′-bipyridine)bis(μ-*N*-(benzyloxycarbonyl)-L-aspartato-*O*,*O*′,*O*″)dicopper(II)–2.5-Water–0.5-Sodium Perchlorate

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The complexes $[Cu(Z\text{-}asp)(H_2O)]_n \cdot 0.25nNaClO_4$ (Z-asp = *N*-(benzyloxycarbonyl)-L-aspartato), $[Cu(Ac\text{-}asp)(H_2O)]_n \cdot nH_2O$ (Ac-Asp = *N*-acetyl-L-aspartato), and $[Cu(Bz\text{-}asp)(H_2O)]_n \cdot 1.5nH_2O$ (Bz-asp = *N*-benzoyl-L-aspartato) were synthesized and characterized by means of spectroscopic and magnetic measurements. The results substantiate dimeric structures of the copper(II) acetate monohydrate type without strong magnetic interactions between the Cu–Cu couples. Mixed complexes with 2,2′-bipyridine were also obtained and characterized. For one of them, $[Cu(Z\text{-}asp)(bpy)]_2 \cdot 2.5H_2O \cdot 0.5NaClO_4$, the crystal structure was determined by X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1$ in a cell of dimensions a = 18.603 (2) Å, b = 12.943 (1) Å, c = 20.945 (2) Å, and β = 106.65 (1)°. The calculated density (1.479 g cm^{-3}) is consistent with four dimeric units in the unit cell. The structure was solved by Patterson and Fourier methods and refined by least-squares calculations to a conventional R factor of 0.078 for 7970 counter data. It consists of two crystallographically independent $Cu_2(Z\text{-}asp)_2(bpy)_2$ molecules, one Na^+ interacting with carboxylate oxygens, a ClO_4^- anion weakly hydrogen bonded to a water molecule, and five lattice water molecules. The binuclear complex molecules result through bridge formation between two metal atoms by the α- and β-carboxylate groups of two aspartate ions. The four copper ions exhibit severely distorted, but similar, square-pyramidal coordination geometries. The aspartate ion, whose β-carboxylate group acts as an axial and equatorial bidentate ligand, shows an unusual metal binding mode, which may be attributed to the presence of Na^+. The crystal packing is determined by hydrogen-bonding interactions and by two different systems of combined ring stacking and hydrophobic interactions involving all the aromatic moieties of the complex molecules. Spectroscopic results suggest that the metal coordination geometry is the same in all the ternary complexes.

Introduction

Side-chain carboxylic groups of biomolecules are important sites for metal binding. However, their involvement in coordination depends on the nature of the other binding sites available for the metal. Particularly, potentially tridentate amino acids with a carboxylic group as the third donor site, such as aspartic and glutamic acids, exhibit only limited tendency to form tridentate chelates in aqueous solution and often coordinate essentially in the bis(glycinato)-like way.[2-5] A similar behavior was observed, in the solid state, with Cu(II) only for highly hydrated ternary complexes existing as isolated monomeric species. In anhydrous or low-hydrate complexes, polymeric chain structures are always present, where aspartate and glutamate ions, in an extended configuration, bridge two or three different copper(II) ions.[6]

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In this context, it could be of interest to observe how the coordination behavior of these ligands may be changed when the amino group, which may be regarded as the primary binding site, is involved in a peptidic bond. Our previous experiences have demonstrated that, due to steric or electronic effects, the introduction of an acetyl, benzoyl, or benzyloxycarbonyl substituent on the amino group of α-amino acids prevents the nitrogen atom from coordinating copper(II).

In this paper we have studied the binary copper(II) complexes of *N*-acetyl, *N*-benzoyl-, and *N*-(benzyloxycarbonyl)aspartic acids and their adducts with 2,2′-bipyridine. The choice of 2,2′-bipyridine as an additional ligand was made by considering the ability of the aromatic moieties to give rise to intra- and intermolecular hydrophobic and stacking interactions, which may be responsible for the occurrence of distinct structures.[7]

Experimental Section

Preparation of Binary Complexes. Cu(Z-asp)·H_2O·0.25$NaClO_4$ was prepared by mixing the monosodium salt of the ligand (10^{-2} mmol/dm^3) and copper(II) perchlorate hydrate (10^{-2} mmol/dm^3) in ethanol. After a few minutes a green compound precipitated from the green solution. Anal. Calcd for $C_{12}H_{13}CuNNa_{0.25}Cl_{0.25}O_8$: C, 38.17; H, 3.91; N, 3.71; H_2O, 4.78. Found: C, 38.80; H, 3.91; N, 3.75; H_2O, 5.01.

Cu(Ac-asp)·2H_2O and Cu(Bz-asp)·2.5H_2O were prepared by dissolving equimolar amounts (10^{-2} mmol/dm^3) of copper(II) acetate hydrate and acid in water and allowing the solution to concentrate at about 50 °C. Anal. Calcd for Cu(Ac-asp)·2H_2O ($C_6H_{11}CuNO_7$): C, 26.43; H, 4.07; N, 5.14; H_2O, 13.21. Found: C, 25.92; H, 3.61; N, 5.09; H_2O, 13.10. Calcd for Cu(Bz-asp)·2.5H_2O ($C_{11}H_{14}CuNO_{7.5}$): C, 38.43; H, 4.10; N, 4.07; H_2O, 13.10. Found: C, 38.02, H, 4.01; N, 3.85; H_2O, 13.00.

Preparation of Ternary Complexes. All the compounds were prepared by dissolving the binary complexes in a methanol–ethanol (1:1 v/v) solution of 2,2′-bipyridine (10^{-2} mmol/dm^3) at a metal to amine molar ratio of 1:1. By evaporation of the solutions at room temperature (~20 °C) blue crystalline compounds separated. Anal. Calcd for Cu(Ac-asp)(bpy)·2H_2O ($C_{16}H_{19}CuN_3O_7$): C, 44.81; H, 4.46; N, 9.80; H_2O, 8.40. Found: C, 44.68; H, 4.52; N, 9.66; H_2O, 8.31. Calcd for Cu(Bz-asp)(bpy)·H_2O ($C_{21}H_{19}CuN_3O_6$): C, 53.33; H, 4.05; N, 8.88; H_2O, 3.81. Found: C, 53.09; H, 3.68; N, 8.85; H, 3.87. Calcd for Cu(Z-asp)(bpy)·$^5/_4$$H_2O$·0.25$NaClO_4$ ($C_{22}H_{21.5}CuN_3Na_{0.25}Cl_{0.25}O_{8.25}$): C, 48.50; H, 3.98; N, 7.72; H_2O, 4.14. Found: C, 47.99; H, 4.01; N, 7.68; H_2O, 4.20.

Collection, Reduction, and Refinement of X-ray Crystallographic Data. The selected crystal, sealed in a glass capillary, was directly mounted in an arbitrary orientation on a Siemens AED automated four-circle diffractometer. All measurements were made at room temperature by using Cu Kα radiation, under the conditions reported in Table I. A survey of the complete data set revealed systematic extinctions compatible for either noncentrosymmetric space group $P2_1$ or centrosymmetric space group $P2_1/m$: this latter was ruled out by considering the presence of optically active L-aspartato ions. Only the observed reflections, not corrected for absorption effects in view of the low absorption coefficient, were used in the structure analysis.

The structure was solved by conventional Patterson and Fourier methods[8] and refined by full-matrix least-squares calculations. The origin of the unit cell was arbitrarily defined by assigning a value of 0.75 to the *y* coordinate of the Cu(1) atom; the enantiomeric model was chosen by assigning the known *S* conformation to the L-aspartate ion.[9] After isotropic refinement for all non-hydrogen atoms, the phenyl carbons were fitted to regular hexagons (C–C : 1.395 Å) and then treated as rigid groups, and the hydrogen atoms of the organic ligands were added to the model in calculated positions (C–H and N–H = 1.0 Å) with isotropic thermal parameters 1.0 Å^2 higher than those of the bonded atoms. Further refinement of this model, in which the Cu, Cl, Na, O, and N atoms were allowed to vibrate anisotropically, led to final convergence at $R = 0.078$ and $R_w = 0.090$ [$w = 0.927/(\sigma^2(F) + 0.0082F_o^2)$]. Because of the large number of variable parameters (763), the atoms have been subdivided into two groups, which have been refined one at a time, in alternate cycles. Least-squares refinement yielded very large thermal motion parameters for the perchlorate atoms, strongly suggesting the presence of disorder, as is usual for this anion. Also, some water oxygens showed unusually high thermal parameters, which could suggest partial site occupancy. Nevertheless, the very expensive computing time prevented any attempt to further investigate the disorder problems. A final difference Fourier synthesis showed no significant residuals, with the exception of some peaks of about 0.70 e Å^{-3} in the perchlorate group region. During refinement, zero weight was assigned to five strong low-order reflections, which may be affected by secondary extinction.

Table I. Crystallographic Data and Summary of Intensity Data Collection[a]

	(A) Crystallographic Parameters		
formula	$C_{88}H_{86}ClCu_4N_{12}NaO_{33}$	β, deg	106.65 (1)
mol wt	2152.37	V, Å^3	4831.7
cryst syst	monoclinic	Z	2
space group	$P2_1$ (C_2^2, No. 4)	d_{calcd}, g/cm^3	1.479
T, K	293	d_{obsd}, g/cm^3	1.48 (2)
a, Å	18.603 (2)	F(000)	2209.9
b, Å	12.943 (1)		
c, Å	20.945 (2)		
	(B) Measurement of Diffraction Data		
radiation (λ, Å)	graphite-monochromated Cu Kα (1.541 78)		
reflcns measd	$\pm h,+k,+l$		
scan type	ω–2θ		
2θ limits, deg	6–120		
lowest scan speed, deg min^{-1}	3.0		
scan width, deg	1.2		
no. of std reflcns	1 every 50 reflcns (no significant changes)		
no. of collcd reflcns	9763		
no. of obsd reflcns	7970 ($I > 2.0\sigma(I)$)		
cryst size, mm	0.35 × 0.23 × 0.20		
abs coeff, cm^{-1}	18.9 (abs cor not applied)		

[a] Unit cell parameters and their esd's were derived from least-squares fits to the setting angles of 27 carefully selected and centered reflections from diverse regions of the reciprocal space.

Complex neutral atom (except for Na$^+$) scattering factors,[10] were used throughout; all calculations were carried out on a VAX 11/750 computer by using the SHELX-76 system of programs[11] and the ORTEP plotting program.[12]

Final atomic positional parameters for the non-hydrogen atoms are reported in Table II.

Physical Measurements. Magnetic susceptibility measurements were obtained on a Newport Instruments (Gouy) balance employing a Newport Instruments cryostatic system, with $HgCo(SCN)_4$ as calibrant, and were corrected for diamagnetism (−116.59 × 10^{-6}, −147.95 × 10^{-6}, and −188.82 × 10^{-6} emu mol^{-1} for Cu(Ac-asp)·2H_2O, Cu(Bz-asp)·2.5H_2O, and Cu(Z-asp)·H_2O·0.25$NaClO_4$, respectively) with the appropriate Pascal constants. Thermogravimetric analyses were carried out at a scan rate of 5 °C min^{-1} on a Mettler TA3000 instrument. X-band ESR spectra (~9.15 GHz) were recorded on a Varian E-9 spectrometer. Electronic spectra were obtained with Varian Cary-2300 (diffuse reflectance and Beckman DU-40 (solution) spectrophotometers.

Results and Discussion

Binary Complexes. The binary complexes form dinuclear units typical of tetracarboxylate-bridged copper(II) complexes, with a water molecule in the axial position of metal coordination, as substantiated by ESR, electronic, and magnetic data (Table III and supplementary material). Interdimeric interactions such to produce magnetic exchange between adjacent Cu–Cu couples are ruled out by the absence of ESR features indicative of delocalization of the triplet state. Therefore, although the ligands most likely act as bridges between adjacent Cu–Cu couples to give infinite chains as in copper(II) succinate dihydrate[13] and the

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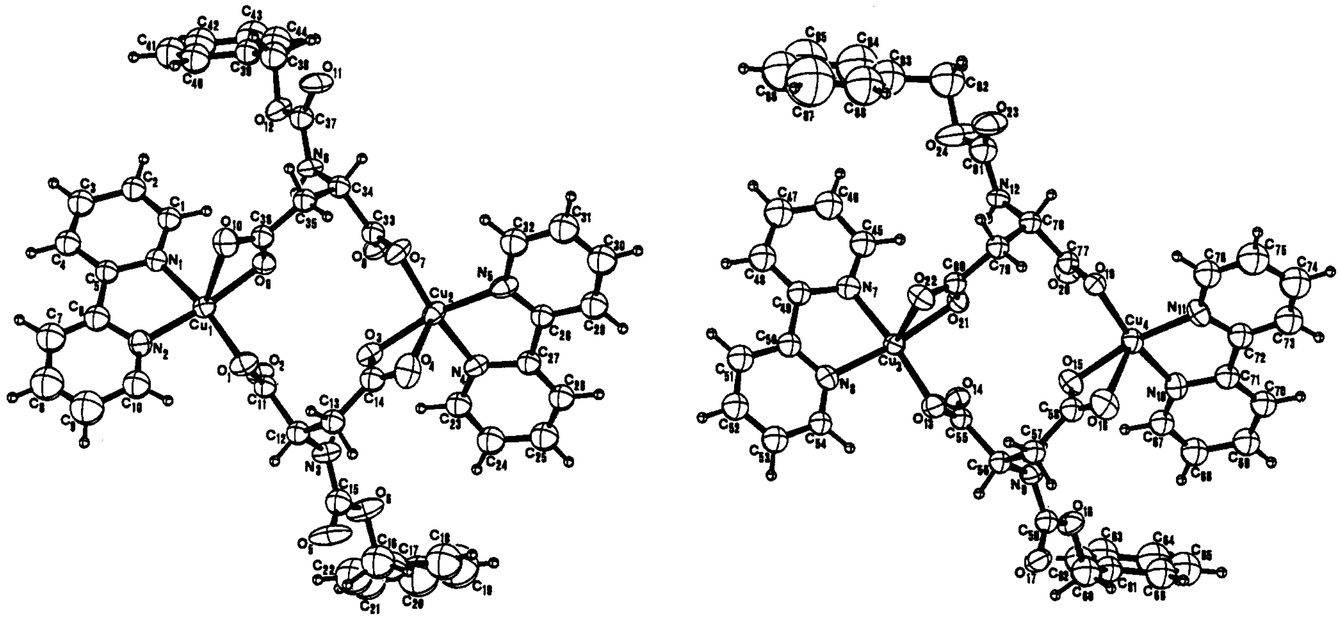

Figure 1. The two crystallographically independent complex molecules with numbering scheme and thermal motion ellipsoids (35%) for non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius.

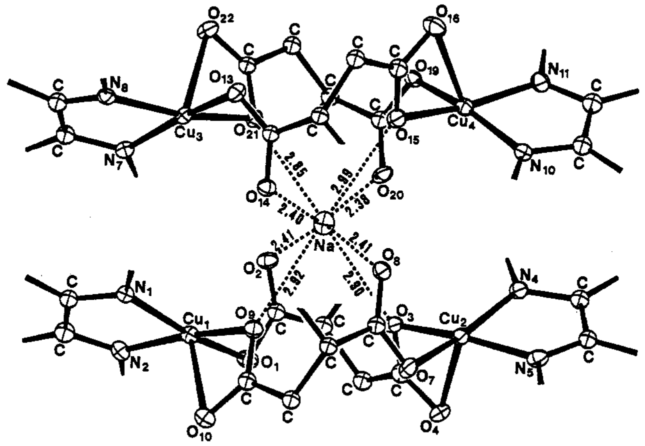

Figure 2. The Na^+ ion environment with Na···O distances (Å).

complexes could be formulated as $[Cu(Z\text{-}asp)(H_2O)]_n \cdot 0.25nNaClO_4$, $[Cu(Ac\text{-}asp)(H_2O)]_n \cdot nH_2O$, and $[Cu(Bz\text{-}asp)(H_2O)_n \cdot 1.5nH_2O$, respectively, the structures may be described as consisting of magnetically isolated dinuclear units.

All the binary complexes easily react with amines, such as 2,2′-bipyridine, to form ternary complexes. In order to gain information about the metal coordination is such complexes and, particularly, to substantiate the ability of substituted aspartic acids to act as bridges between metal ions as well as to evaluate the contribution of stacking interactions (if present), the crystal and molecular structure of $[Cu(Z\text{-}asp)(bpy)]_2 \cdot 2.5H_2O \cdot 0.5NaClO_4$ was determined.

Description of the Structure of $[Cu(Z\text{-}asp)(bpy)]_2 \cdot 2.5H_2O \cdot 0.5NaClO_4$. Table IV contains selected bond lengths and bond angles, with atoms numbered as in Figure 1.

The structure is built up by two crystallographically independent $[Cu_2(Z\text{-}asp)_2(bpy)_2]$ units, while Na^+ strongly interacts with uncoordinated carboxylate oxygens (Figure 2), the ClO_4^- anion is weakly hydrogen-bonded to a water molecule, and five water molecules are in the lattice and contribute to the overall crystalline stability through hydrogen-bonding interactions. Further contributions to the crystal packing forces are ascribed to ring-stacking interactions involving all the aromatic moieties of the complex binuclear molecules (Figure 3).

The dimeric molecules result from double-bridge formation between two copper ions by the α- and β-carboxylate groups of two aspartate ions. The dimensions of the two complex molecules,

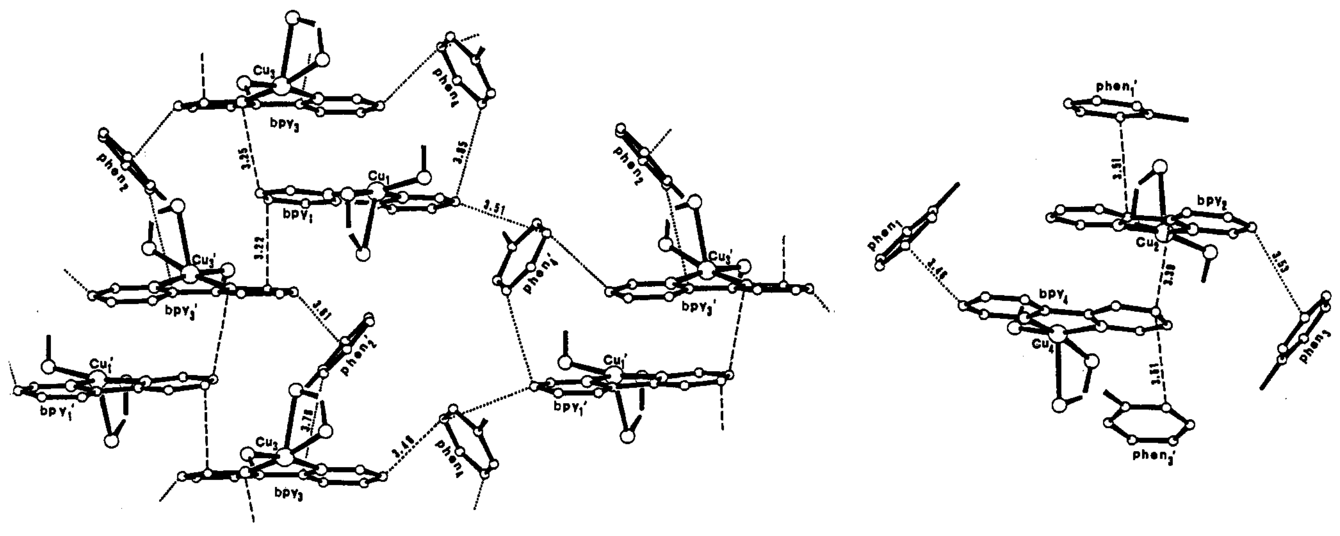

Figure 3. Ring-stacking (dashed lines) and hydrophobic (dotted lines) interactions between aromatic moieties with shortest interatomic separations (Å).

Table II. Final Fractional Coordinates with Esd's in Parentheses[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu(1)	0.77059 (7)	0.75	0.66313 (6)	Cu(3)	0.59070 (8)	0.0343 (1)	0.58964 (6)
Cu(2)	0.80067 (6)	0.8526 (1)	0.94823 (6)	Cu(4)	0.68272 (8)	0.2009 (1)	0.87857 (7)
N(1)	0.6784 (4)	0.7433 (6)	0.5853 (4)	N(7)	0.6601 (4)	−0.0001 (6)	0.5359 (4)
C(1)	0.6063 (5)	0.7554 (9)	0.5864 (5)	C(45)	0.7351 (6)	−0.0021 (9)	0.5575 (6)
C(2)	0.5472 (6)	0.7486 (9)	0.5303 (5)	C(46)	0.7790 (7)	−0.021 (1)	0.5157 (6)
C(3)	0.5635 (6)	0.732 (1)	0.4678 (6)	C(47)	0.7430 (7)	−0.039 (1)	0.4496 (7)
C(4)	0.6343 (6)	0.7199 (9)	0.4666 (5)	C(48)	0.6640 (7)	−0.036 (1)	0.4252 (6)
C(5)	0.6924 (5)	0.7261 (7)	0.5266 (5)	C(49)	0.6255 (5)	−0.0143 (8)	0.4700 (5)
C(6)	0.7734 (6)	0.718 (1)	0.5303 (6)	C(50)	0.5410 (5)	−0.0134 (9)	0.4542 (5)
C(7)	0.8003 (8)	0.702 (1)	0.4788 (7)	C(51)	0.4924 (6)	−0.019 (1)	0.3870 (6)
C(8)	0.878 (1)	0.703 (2)	0.4888 (9)	C(52)	0.4171 (7)	−0.020 (1)	0.3787 (6)
C(9)	0.923 (1)	0.721 (2)	0.5461 (9)	C(53)	0.3904 (7)	−0.016 (1)	0.4322 (6)
C(10)	0.8930 (7)	0.731 (1)	0.6026 (7)	C(54)	0.4405 (5)	−0.0086 (8)	0.4946 (5)
N(2)	0.8214 (5)	0.7337 (7)	0.5929 (4)	N(8)	0.5133 (4)	−0.0063 (6)	0.5050 (4)
O(1)	0.8640 (4)	0.7859 (6)	0.7283 (4)	O(13)	0.5179 (3)	0.0436 (6)	0.6402 (3)
O(2)	0.8113 (3)	0.9403 (5)	0.7177 (3)	O(14)	0.5862 (3)	−0.0777 (5)	0.7018 (3)
C(11)	0.8630 (5)	0.8818 (8)	0.7423 (5)	C(55)	0.5345 (4)	−0.0114 (7)	0.6900 (4)
C(12)	0.9349 (5)	0.9199 (8)	0.7931 (5)	C(56)	0.4872 (5)	0.0039 (7)	0.7380 (4)
C(13)	0.9603 (6)	0.8469 (9)	0.8520 (5)	C(57)	0.4822 (5)	0.1185 (8)	0.7557 (5)
C(14)	0.9046 (6)	0.8354 (9)	0.8925 (5)	C(58)	0.5538 (5)	0.1633 (8)	0.8004 (5)
O(3)	0.8396 (3)	0.8796 (5)	0.8706 (3)	O(15)	0.6133 (4)	0.1104 (5)	0.8128 (3)
O(4)	0.9229 (5)	0.7874 (7)	0.9467 (4)	O(16)	0.5513 (5)	0.2512 (7)	0.8249 (5)
N(3)	0.9268 (4)	1.0251 (6)	0.8136 (4)	N(9)	0.5113 (4)	−0.0606 (6)	0.7963 (3)
C(15)	0.9857 (6)	1.089 (1)	0.8318 (6)	C(59)	0.4634 (5)	−0.1020 (8)	0.8258 (5)
O(5)	1.0493 (4)	1.0689 (8)	0.8367 (6)	O(17)	0.3948 (4)	−0.0863 (7)	0.8097 (4)
O(6)	0.9607 (4)	1.1842 (6)	0.8477 (5)	O(18)	0.4988 (4)	−0.1666 (6)	0.8754 (3)
C(16)	1.019 (1)	1.259 (2)	0.866 (1)	C(60)	0.4531 (8)	−0.222 (1)	0.9086 (7)
C(17)	0.9818 (6)	1.3636 (9)	0.8635 (6)	C(61)	0.4979 (5)	−0.2914 (7)	0.9586 (4)
C(18)	0.9681 (6)	1.4060 (9)	0.9201 (6)	C(62)	0.5249 (5)	−0.3824 (7)	0.9382 (4)
C(19)	0.9345 (6)	1.5031 (9)	0.9168 (6)	C(63)	0.5693 (5)	−0.4494 (7)	0.9854 (4)
C(20)	0.9147 (6)	1.5576 (9)	0.8568 (6)	C(64)	0.5868 (5)	−0.4254 (7)	1.0531 (4)
C(21)	0.9283 (6)	1.5151 (9)	0.8002 (6)	C(65)	0.5598 (5)	−0.3344 (7)	1.0735 (4)
C(22)	0.9619 (6)	1.4181 (9)	0.8036 (6)	C(66)	0.5154 (5)	−0.2674 (7)	1.0263 (4)
N(4)	0.8405 (4)	0.9845 (6)	0.9919 (4)	N(10)	0.6683 (5)	0.1259 (7)	0.9570 (4)
C(23)	0.8648 (6)	1.0652 (9)	0.9638 (6)	C(67)	0.6361 (6)	0.0343 (9)	0.9576 (5)
C(24)	0.8946 (7)	1.151 (1)	0.9990 (6)	C(68)	0.6291 (7)	−0.011 (1)	1.0134 (6)
C(25)	0.9009 (7)	1.157 (1)	1.0677 (6)	C(69)	0.6590 (6)	0.037 (1)	1.0745 (6)
C(26)	0.8779 (6)	1.0745 (9)	1.0963 (6)	C(70)	0.6928 (6)	0.132 (1)	1.0764 (6)
C(27)	0.8476 (5)	0.9916 (9)	1.0596 (5)	C(71)	0.6962 (6)	0.1763 (9)	1.0162 (5)
C(28)	0.8161 (5)	0.8982 (8)	1.0833 (5)	C(72)	0.7295 (6)	0.2804 (9)	1.0109 (5)
C(29)	0.8175 (7)	0.888 (1)	1.1513 (6)	C(73)	0.7596 (7)	0.348 (1)	1.0624 (7)
C(30)	0.7843 (8)	0.798 (1)	1.1671 (8)	C(74)	0.7886 (9)	0.436 (1)	1.0512 (8)
C(31)	0.7533 (8)	0.724 (1)	1.1218 (7)	C(75)	0.7881 (9)	0.466 (2)	0.9859 (8)
C(32)	0.7551 (7)	0.740 (1)	1.0563 (6)	C(76)	0.7613 (7)	0.397 (1)	0.9386 (7)
N(5)	0.7873 (5)	0.8275 (6)	1.0380 (4)	N(11)	0.7303 (5)	0.3041 (7)	0.9481 (4)
O(7)	0.7395 (4)	0.7352 (6)	0.9061 (3)	O(19)	0.7222 (5)	0.2642 (7)	0.8121 (5)
O(8)	0.6681 (4)	0.8595 (5)	0.8476 (3)	O(20)	0.7786 (4)	0.1140 (5)	0.8102 (3)
C(33)	0.6851 (5)	0.7675 (7)	0.8604 (5)	C(77)	0.7600 (5)	0.2023 (8)	0.7897 (4)
C(34)	0.6366 (5)	0.6798 (8)	0.8197 (4)	C(78)	0.7825 (5)	0.2451 (8)	0.7284 (4)
C(35)	0.6865 (5)	0.6028 (8)	0.7962 (5)	C(79)	0.7125 (5)	0.2811 (8)	0.6743 (5)
C(36)	0.7171 (5)	0.6446 (8)	0.7419 (5)	C(80)	0.6619 (5)	0.1959 (7)	0.6359 (4)
O(9)	0.7160 (3)	0.7430 (6)	0.7309 (3)	O(21)	0.6695 (3)	0.1039 (5)	0.6616 (3)
O(10)	0.7449 (4)	0.5827 (7)	0.7084 (4)	O(22)	0.6134 (4)	0.2168 (5)	0.5842 (3)
N(6)	0.5759 (4)	0.7202 (6)	0.7660 (4)	N(12)	0.8251 (5)	0.1718 (7)	0.7028 (5)
C(37)	0.5064 (5)	0.6795 (8)	0.7477 (5)	C(81)	0.8790 (7)	0.203 (1)	0.6754 (6)
O(11)	0.4895 (4)	0.5991 (6)	0.7732 (4)	O(23)	0.8914 (5)	0.2928 (7)	0.6634 (6)
O(12)	0.4583 (4)	0.7359 (6)	0.7013 (4)	O(24)	0.9158 (6)	0.1186 (9)	0.6612 (7)
C(38)	0.3814 (6)	0.703 (1)	0.6849 (6)	C(82)	0.983 (1)	0.140 (2)	0.6433 (9)
C(39)	0.3350 (4)	0.7730 (7)	0.6336 (3)	C(83)	0.965 (1)	0.099 (2)	0.5713 (7)
C(40)	0.3333 (4)	0.7620 (7)	0.5669 (3)	C(84)	0.995 (1)	0.010 (2)	0.5520 (7)
C(41)	0.2881 (4)	0.8269 (7)	0.5187 (3)	C(85)	0.977 (1)	−0.017 (2)	0.4848 (7)
C(42)	0.2445 (4)	0.9027 (7)	0.5371 (3)	C(86)	0.929 (1)	0.045 (2)	0.4369 (7)
C(43)	0.2462 (4)	0.9136 (7)	0.6038 (3)	C(87)	0.899 (1)	0.134 (2)	0.4561 (7)
C(44)	0.2915 (4)	0.8488 (7)	0.6520 (3)	C(88)	0.917 (1)	0.161 (2)	0.5233 (7)
Ow(25)	0.7071 (7)	0.576 (1)	0.2369 (6)	Ow(28)	0.562 (1)	0.894 (1)	0.222 (2)
Ow(26)	0.8141 (7)	0.484 (1)	0.6218 (5)	Ow(29)	0.6945 (9)	0.756 (2)	0.3119 (8)
Ow(27)	0.149 (1)	−0.004 (2)	0.761 (1)	Na	0.7114 (2)	0.9596 (3)	0.7688 (2)
Cl	0.1259 (4)	0.7184 (6)	0.7402 (3)	O(30)	0.196 (1)	0.704 (3)	0.759 (2)
O(31)	0.108 (2)	0.765 (3)	0.7933 (9)	O(32)	0.117 (1)	0.773 (3)	0.6857 (9)
O(33)	0.122 (3)	0.613 (2)	0.744 (2)				

[a] Phenyl rings [C(17)–C(22), C(39)–C(44), C(61)–C(66), C(83)–C(88)] were treated as rigid groups of D_{6h} idealized geometry and C–C distances of 1.395 Å.

both showing approximate C_2 symmetry, are similar. The four metal atoms display severely distorted, but similar, square-pyramidal coordination geometries, the donor atoms being two bpy nitrogens, one α-carboxylate oxygen and one β-carboxylate oxygen in the equatorial plane, and the second oxygen of a bidentate β-carboxylate function in the apical position. The largest dis-

Table III. Spectroscopic and Magnetic Data for the Complexes

	solid state					solution[a]				
compd	$\bar{\nu}_{max}$, 10^3 cm^{-1}	$g_\parallel$	$g_\perp$	D, cm^{-1}	$-2J$ cm^{-1}	solvent	$\bar{\nu}_{max}$, 10^3 cm^{-1}	$g_\parallel$	$g_\perp$	$A_\parallel$, 10^{-4} cm^{-1}
$[Cu(Z\text{-}asp)(H_2O)]_n \cdot 0.25n NaClO_4$	14.1	2.39	2.08	0.35	309.8 ± 13					
$[Cu(Ac\text{-}asp)(H_2O)]_n \cdot nH_2O$	14.0	2.40	2.09	0.35	332.5 ± 17					
$[Cu(Bz\text{-}Asp)(H_2O)]_n \cdot 1.5nH_2O$	13.4	2.38	2.08	0.35	327.3 ± 6					
$[Cu(Z\text{-}asp)(bpy)]_2 \cdot 2.5H_2O \cdot 0.5NaClO_4$	15.0, 17.2 sh					Me_2SO	15.3	2.290	2.060	178
$[Cu(Ac\text{-}asp)(bpy)] \cdot 2H_2O$	15.1, 17.0 sh	2.23	2.07			CH_3OH	15.4	2.289	2.066	178
$[Cu(Bz\text{-}asp)(bpy)] \cdot H_2O$	15.1, 17.0 sh	2.23	2.07			CH_3OH	15.5	2.277	2.066	177

[a] ESR spectra recorded at 120 K.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg)

Cu(1)–N(1)	2.000 (6)	Cu(3)–N(7)	1.992 (9)
Cu(1)–N(2)	1.98 (1)	Cu(3)–N(8)	2.006 (7)
Cu(1)–O(1)	1.934 (6)	Cu(3)–O(13)	1.947 (7)
Cu(1)–O(9)	1.969 (8)	Cu(3)–O(21)	1.991 (5)
Cu(1)–O(10)	2.465 (9)	Cu(3)–O(22)	2.409 (7)
Cu(2)–N(4)	1.979 (8)	Cu(4)–N(10)	1.990 (9)
Cu(2)–N(5)	1.99 (1)	Cu(4)–N(11)	1.987 (8)
Cu(2)–O(7)	1.951 (7)	Cu(4)–O(19)	1.93 (1)
Cu(2)–O(3)	1.992 (7)	Cu(4)–O(15)	1.979 (6)
Cu(2)–O(4)	2.43 (1)	Cu(4)–O(16)	2.467 (8)
C(12)–N(3)	1.45 (1)	C(56)–N(9)	1.44 (1)
N(3)–C(15)	1.34 (1)	N(9)–C(59)	1.33 (1)
C(15)–O(5)	1.19 (1)	C(59)–O(17)	1.24 (1)
C(15)–O(6)	1.39 (1)	C(59)–O(18)	1.35 (1)
O(6)–C(16)	1.43 (2)	O(18)–C(60)	1.43 (2)
C(34)–N(6)	1.44 (1)	C(78)–N(12)	1.44 (1)
N(6)–C(37)	1.35 (1)	N(12)–C(81)	1.35 (2)
C(37)–O(11)	1.25 (1)	C(81)–O(23)	1.23 (2)
C(37)–O(12)	1.34 (1)	C(81)–O(24)	1.36 (2)
O(12)–C(38)	1.44 (1)	O(24)–C(82)	1.44 (2)
N(1)–Cu(1)–N(2)	82.5 (3)	N(7)–Cu(3)–N(8)	81.9 (3)
N(1)–Cu(1)–O(1)	166.6 (3)	N(7)–Cu(3)–O(13)	170.4 (3)
N(1)–Cu(1)–O(9)	95.0 (3)	N(7)–Cu(3)–O(21)	94.2 (3)
N(1)–Cu(1)–O(10)	93.4 (3)	N(7)–Cu(3)–O(22)	92.3 (3)
N(2)–Cu(1)–O(1)	91.5 (3)	N(8)–C1(3)–O(13)	93.5 (3)
N(2)–Cu(1)–O(9)	171.0 (4)	N(8)–Cu(3)–O(21)	166.6 (3)
N(2)–Cu(1)–O(10)	112.3 (4)	N(8)–Cu(3)–O(22)	107.8 (3)
O(1)–Cu(1)–O(9)	92.7 (3)	O(13)–Cu(3)–O(21)	92.1 (3)
O(1)–Cu(1)–O(10)	100.0 (3)	O(13)–Cu(3)–O(22)	97.1 (3)
O(9)–Cu(1)–O(10)	59.1 (3)	O(21)–Cu(3)–O(22)	59.4 (2)
Cu(1)–N(1)–C(1)	127.0 (6)	Cu(3)–N(7)–C(45)	126.5 (7)
Cu(1)–N(1)–C(5)	114.0 (6)	Cu(3)–N(7)–C(49)	114.1 (6)
Cu(1)–N(2)–C(6)	114.0 (8)	Cu(3)–N(8)–C(50)	112.7 (6)
Cu(1)–N(2)–C(10)	125.4 (8)	Cu(3)–N(8)–C(54)	126.8 (7)
Cu(1)–O(1)–C(11)	109.1 (5)	Cu(3)–O(13)–C(55)	112.4 (6)
Cu(1)–O(9)–C(36)	101.0 (7)	Cu(3)–O(21)–C(80)	97.7 (4)
Cu(1)–O(10)–C(36)	79.2 (6)	Cu(3)–O(22)–C(80)	80.6 (6)
N(4)–Cu(2)–N(5)	80.5 (3)	N(10)–Cu(4)–N(11)	81.9 (4)
N(4)–Cu(2)–O(7)	166.9 (3)	N(10)–Cu(4)–O(19)	165.9 (3)
N(4)–Cu(2)–O(3)	92.9 (3)	N(10)–Cu(4)–O(15)	94.0 (3)
N(4)–Cu(2)–O(4)	94.4 (3)	N(10)–Cu(4)–O(16)	98.9 (3)
N(5)–Cu(2)–O(7)	95.0 (3)	N(11)–Cu(4)–O(19)	93.6 (4)
N(5)–Cu(2)–O(3)	166.4 (3)	N(11)–Cu(4)–O(15)	166.5 (4)
N(5)–Cu(2)–O(4)	109.0 (3)	N(11)–Cu(4)–O(16)	109.3 (3)
O(7)–Cu(2)–O(3)	93.9 (3)	O(19)–Cu(4)–O(15)	93.3 (3)
O(7)–Cu(2)–O(4)	98.6 (3)	O(19)–Cu(4)–O(16)	95.2 (3)
O(3)–Cu(2)–O(4)	59.4 (3)	O(15)–Cu(4)–O(16)	58.3 (3)
Cu(2)–N(4)–C(23)	126.7 (7)	Cu(4)–N(10)–C(67)	127.6 (7)
Cu(2)–N(4)–C(27)	116.2 (7)	Cu(4)–N(10)–C(71)	114.2 (7)
Cu(2)–N(5)–C(28)	115.6 (7)	Cu(4)–N(11)–C(72)	115.7 (7)
Cu(2)–N(5)–C(32)	125.1 (8)	Cu(4)–N(11)–C(76)	126.8 (8)
Cu(2)–O(7)–C(33)	109.0 (6)	Cu(4)–O(19)–C(77)	111.8 (7)
Cu(2)–O(3)–C(14)	98.9 (6)	Cu(4)–O(15)–C(58)	100.5 (6)
Cu(2)–O(4)–C(14)	80.1 (7)	Cu(4)–O(16)–C(58)	78.4 (6)

tortions from ideal square-pyramidal coordination geometry appear mainly due to geometrical constraints due to the bidentate carboxylate groups, with O–Cu–O bond angles ranging from 58.3 (3) to 59.4 (3)° and Cu–O(apical) bond distances in the 2.409 (7)–2.467 (8) Å range. The basal coordination planes are tetrahedrally distorted, with atomic deviations from best fit planes in the 0.161–0.223-Å range. The copper ions lie on their basal coordination planes (maximum deviation 0.040 Å) and are not displaced toward the apical donors, as is usually observed and expected for this Cu^{2+} stereochemistry.[14] The closest approaches to the sixth octahedral position about the copper atoms involve α-carboxylate oxygens, but their interatomic separations (from 2.73 to 2.82 Å) and the subtended O–Cu–O angles (from 51.5 to 53.3°) may be associated with only weak axial nonbonding interactions.[15] Furthermore, it may be outlined that all these carboxylate oxygens are involved in strong interactions (from 2.385 (8) to 2.411 (8) Å) with the Na^+ ion (see Figure 2).

There are not significant differences between the dimensions of the four independent *N*-(benzyloxycarbonyl)-L-aspartato anions, whose individual and mean bond distances are in the usual ranges.[6,16] As expected, they bind copper(II) only through carboxylate groups, contrary to the unsubstituted derivatives where the availability of the amino group leads to metal chelation. Previous structural investigations on unsubstituted L-aspartato and L-glutamato copper(II) complexes[6] have always shown unidentate or syn–anti bridging α-carboxylate groups and unidentate or uncoordinated β- or γ-carboxylate functions, giving rise to one- or two-dimensional polymeric structures or to mononuclear species. Furthermore, the formation of binuclear Cu(II) complexes with N-substituted amino acids was observed to occur through syn–syn carboxylate bridges, leading to the dimeric cupric acetate structure,[17] or, more rarely, through bridging monodentate carboxylate oxygens.[6,15] The presence of Na^+ ions, whose closest interactions (similar to those in many reported structures) involve the uncoordinated α-carboxylate oxygens (which have the largest formal negative charge in the complex), could be important in determining the coordination mode of the ligand.

The crystal packing of the complex molecules is mainly determined by an infinite three-dimensional network of hydrogen-bonding interactions involving carboxylate oxygens, amino groups, and water molecules, with N···O or O···O separations in the 2.76–3.19-Å range. Furthermore, all the aromatic moieties of the complex molecules take part in nonbonding ring–ring interactions. These interactions, observed either in solution or in the solid state, are known to enhance the stability of mixed-ligand ternary complexes.[6,16,20-23] The aromatic moieties of the present compound give rise to two very different systems of combined ring-stacking and hydrophobic interactions (see Figure 3). In the first, strong ring-stacking interactions between bpy ligands of two binuclear units tie the complex molecules in infinite chains, running

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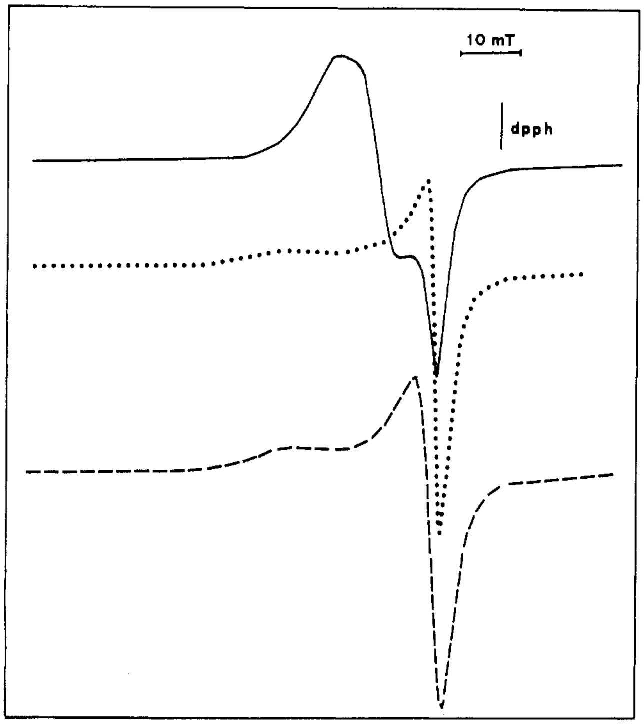

Figure 4. X-Band ESR spectra of $[Cu(Z\text{-}asp)(bpy)]_2{\cdot}2.5H_2O{\cdot}0.5NaClO_4$ (—), $[Cu(Ac\text{-}asp)(bpy)]{\cdot}2H_2O$ (···), and $[Cu(Bz\text{-}asp)(bpy)]{\cdot}H_2O$ (- - -).

parallel to the *b* cell axis. These chains are bridged through hydrophobic interactions between bpy molecules and phenyl groups. A comparison with previous structural results[7,20–22] shows very short interatomic distances (3.22 and 3.25 Å) between ring-stacked bpy moieties, whose mean planes make dihedral angles of 1.9 and 16.7°, respectively. The second system of nonbonding ring–ring interactions involves ring-stacking interactions of the $A_1{\cdots}B_1{\cdots}B_2{\cdots}A_2$ type (A = phenyl, B = bpy) and hydrophobic contacts between bpy ligands and other phenyl groups. The shortest interatomic separations between rings and the dihedral angles between stacked ring planes are in the ranges 3.39–3.53 Å and 2.3–11.5°, respectively.

Spectroscopic Properties of Ternary Complexes. The powder ESR spectrum of $[Cu(Z\text{-}asp)(bpy)]_2{\cdot}2.5H_2O{\cdot}0.5NaClO_4$ (Figure 4) is rather uninformative as likely affected by either exchange interactions or misalignment of the molecular axes, whereas the electronic absorption spectrum (Table III) is consistent with the square-pyramidal coordination of the metal atom.[24] The other ternary complexes exhibit ESR spectra (Figure 4) which, although again suggestive of weak coupling between the metal centers, as judged by the small line width, support a strongly distorted tetragonal coordination involving nitrogen donors in the metal plane. Instead, the electronic spectra are similar to that of $[Cu(Z\text{-}asp)(bpy)_2]_2{\cdot}2.5H_2O{\cdot}0.5NaClO_4$ (Table III). Thus, on the whole, the spectroscopic results suggest that all the adducts have similar coordination geometry and involve the same donor set.

Dissolution of the complexes yields spectral parameters (Table III) that suggest an increase of the axial perturbation, compared to that in the solid state, due to the presence of oxygen donors in the apical positions of a CuN_2O_2-based chromophore. Particularly, the ESR parameters agree very well with those found, in either solution or solid state, for copper(II) ternary complexes of tridentate O donors and 2,2′-bipyridine containing a water molecule in the sixth position.[25]

Registry No. $[Cu(Z\text{-}asp)(H_2O)]_n$, 102922-19-0; $[Cu(Ac\text{-}asp)(H_2O)]_n$, 102922-21-4; $[Cu(Bz\text{-}asp)(H_2O)]_n$, 102922-23-6; Cu(Ac-asp)(bpy), 102922-24-7; Cu(Bz-asp)(bpy), 102922-25-8; $Cu(Z\text{-}asp)(bpy){\cdot}{}^5/_2H_2O{\cdot}0.25NaClO_4$, 102922-27-0.

Supplementary Material Available: Listings of anisotropic temperature factors, isotropic thermal factors, positional and isotropic thermal parameters for the hydrogen atoms, interatomic distances and angles, nonbonding ring–ring interactions, least-squares planes for $[Cu(Z\text{-}asp)(bpy)]_2{\cdot}2.5H_2O{\cdot}0.5NaClO_4$, and variable-temperature magnetic data for the binary complexes (11 pages). Ordering information is given on any current masthead page.

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Exceptionally Variable Solvatochromism of Centrosymmetric Octacarbonyldimolybdenum(0) Complexes. Rules to Estimate the Solvent Sensitivity of Charge-Transfer Absorption Energies

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Solvent sensitivities varying by a factor of more than 6 were observed for the metal-to-ligand charge-transfer (MLCT, $\pi^* \leftarrow d$) absorption bands in four $(\mu\text{-L})[Mo(CO)_4]_2$ complexes where μ-L are the doubly bidentate bridging ligands 2,2′-bipyrimidine (bpym), 2,5-bis(2-pyridyl)pyrazine (dppz), 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (dptz), and azo-2,2′-bipyridine (abpy). Although the binuclear complexes are centrosymmetric and should, therefore, not possess a permanent dipole moment, they exhibit stronger solvatochromism than their mononuclear, noncentrosymmetric analogues. The highly variable solvatochromic behavior of these complexes may be understood by considering the importance of dispersion interactions in such complexes; changes in molecular polarizability between the respective ground and MLCT excited states depend strongly on the differences in σ donation from the α-diimine ligand in the neutral and anion radical forms and on the possible degeneracy of the ligand π* molecular orbitals. Some general guidelines are given that allow us to estimate the extent of MLCT absorption band solvent sensitivities from the properties of the ligands and of the metal fragments.

Introduction

After several earlier studies of the solvatochromic behavior of group 6 metal complexes with α-diimine ligands,[1–10] this phenomenon[11–13] has received some renewed attention in connection with approaches toward a more detailed understanding of bonding, electron transfer, and photoreactivity in such compounds.[14–24]

[†] Karl Winnacker Fellow, 1982–1987.

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