Na^+ interaction very similar to that with Ni(salen). Similar explanations are reported in literature to explain why the Ni complexes with high steric hindrance are unable to form associated species or to coordinate two molecules of pyridine giving the octahedral complex $Ni(SB–R)_2 \cdot 2Py$.[22]

Acknowledgment. This work was supported by the Consiglio Nazionale delle Ricerche and the Ministero delle Pubblica Istruzione, Roma, Italy. We also wish to thank ENI for a fellowship awarded to R.S.

Registry No. NH_4^+, 14798-03-9; $EtNH_3^+$, 16999-99-8; $Et_2NH_2^+$, 19497-23-5; Et_3NH^+, 17440-81-2; *m*-$C_7H_{15}NH_3^+$, 21005-96-9; $C(NH_2)_3^+$, 25215-10-5; $N_2H_6^{2+}$, 31479-14-8; $H_3N(CH_2)_8NH_3^{2+}$, 49745-06-4; Na, 7440-23-5.

---

[22] Holm, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 4683. Shumann, M.; Holturn, A.; Wannowius, J.; Elias, H. *Inorg. Chem.* **1982**, *21*, 606.

Contribution from the Dipartimento di Chimica Analitica, Università di Torino, 10125 Torino, Italy,
Istituto di Chimica Generale, Inorganica e Analitica, Università di Cagliari, 09124 Cagliari, Italy,
and Dipartimento di Scienze Chimiche, Università di Catania, 95125 Catania, Italy

Ligand–Ligand Interactions in Metal Complexes. Thermodynamic and Spectroscopic Investigation of Simple and Mixed Copper(II) and Zinc(II) Substituted-Malonate Complexes with 2,2′-Bipyridyl in Aqueous Solution

Paola Amico,[1a] Raffaele P. Bonomo,*[1b] Rosario Calì,[1c] Vincenzo Cucinotta,[1c] Pier G. Daniele,*[1a]
Giorgio Ostacoli,[1a] and Enrico Rizzarelli*[1c]

Received October 12, 1988

The influence of side-chain residues on the thermodynamic properties of simple and mixed complexes has been investigated by potentiometric and calorimetric methods for ML, ML_2, and M(bpy)(L), where M = Cu(II) and Zn(II), bpy = 2,2′-bipyridyl, and L = malonate, methylmalonate, *n*-propylmalonate, isopropylmalonate, *n*-butylmalonate, isobutylmalonate, dimethylmalonate, di-*n*-propylmalonate, and di-*n*-butylmalonate. The presence of noncovalent ligand–ligand interaction is indicated by a more favorable enthalpy change accompanying the complex formation of mixed zinc(II)–2,2′-bipyridyl species with *n*-propyl-, isobutyl-, *n*-butyl-, di-*n*-propyl- and di-*n*-butylmalonates. The EPR parameters of mixed copper(II) complexes show that the metal ion reaches the same geometry and coordination number with little or no influence of side-chain groups. This result together with the thermodynamic data indicates that, in the mixed copper(II) complex, solvophobic ligand–ligand interaction is not present. The diagnostic character of a thermodynamic approach is confirmed by ^1H NMR data on mixed zinc(II) complexes, which show an upfield shift only for those species having more exothermic $\Delta H°$ formation values.

Introduction

Noncovalent interactions between molecules or side-chain groups of macromolecules are known to provide the specificity and flexibility required in most important biological processes[2–10] and have been also invoked to explain drug biological activity.[11] Many model systems have been studied, such as molecules of low molecular weight containing nucleic acid bases connected by polymethylene chains.[12] Analogously, since indirect interactions mediated through metal cations have been found in biological systems,[13–15] a number of metal complexes with noncovalent interactions between side-chain groups have been investigated.[16–22] In the model systems the above-mentioned interactions play an important role, providing distinct features in stability,[23] reactivity,[24] selective synthesis,[25] racemate resolution,[26] and thermodynamic stereoselectivity.[27,28]

On the basis of calorimetric data and EPR parameters, we revealed the presence of side-chain interactions in mixed complexes of metal ions containing ATP and amino acids[29,30] or biofunctional ligands such as histamine[31] and in copper(II) complexes of linear dipeptides.[32] The enthalpy change was found to become more favorable and the entropy change less favorable if the side chains

---

(1) (a) Università di Torino. (b) Università di Cagliari. (c) Università di Catania.
(2) Frieden, E. *J. Chem. Educ.* **1975**, *52*, 754.
(3) Hélène, C. *Stud. Biophys.* **1976**, *57*, 211.
(4) Hélène, C.; Lancelot, G. *Prog. Biophys. Mol. Biol.* **1982**, *39*, 1.
(5) Lohman, T. M.; De Haseth, P. L.; Record, M. T., Jr. *Biochemistry* **1980**, *19*, 3522.
(6) Behmoaras, T.; Toulme, J. J.; Hélène, C. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 926.
(7) Saenger, W. *Principles of Nucleic Acid Structure*; Springer-Verlag: New York, 1984.
(8) Cantor, C. R.; Schimmel, P. R. *Biophysical Chemistry*; W. H. Freeman: San Francisco, 1982.
(9) Lipscomb, W. N. *Acc. Chem. Res.* **1970**, *3*, 81.
(10) Jencks, W. P. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1975**, *43*, 219.
(11) Delben, F.; Quadrifoglio, F.; Crescenzi, V. *Biopolymers* **1982**, *21*, 331.
(12) Leonard, N. J. *Acc. Chem. Res.* **1979**, *12*, 424.
(13) Hélène, C. *Nucl. Acids Res.* **1975**, *2*, 961.
(14) Lipscomb, W. N.; Reeke, G. N.; Hartsuck, J. A.; Quiocho, F. A.; Bethge, P. H. *Philos. Trans. R. Soc. London, B* **1970**, *257*, 177.
(15) Arnone, A.; Bier, C. J.; Cotton, F. A.; Day, V. W.; Hazen, E. E.; Richardson, D. C.; Yonath, A. *J. Biol. Chem.* **1971**, *246*, 2302.
(16) Sigel, H. In *Coordination Chemistry-20*; Banerjea, D., Ed.; Pergamon Press: New York, 1980; p 27.
(17) Sigel, H.; Fischer, B. E.; Farkas, E. *Inorg. Chem.* **1983**, *22*, 925.
(18) Yamauchi, O. *J. Mol. Catal.* **1984**, *23*, 255.
(19) Yamauchi, O. *Inorg. Chim. Acta* **1985**, *100*, 165.
(20) Sigel, H.; Malini-Balakrishnan, R.; Haring, U. K. *J. Am. Chem. Soc.* **1985**, *107*, 5137.
(21) Sigel, H.; Scheller-Krattiger, K. H.; Prijs, B. *J. Am. Chem. Soc.* **1986**, *108*, 4171.
(22) Arena, G.; Rizzarelli, E. In *Metal Complexes In Solution*; Jenne, E. A., Rizzarelli, E., Romano, V., Sammartano, S., Eds.; Piccin: Padua, Italy, 1986; p 105.
(23) Mitchell, P. R.; Prijs, B.; Sigel, H. *Helv. Chim. Acta* **1979**, *62*, 1723.
(24) Cayley, G. R.; Margerum, D. W. *J. Chem. Soc., Chem. Commun.* **1974**, 1002.
(25) Nakamura, M.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3377.
(26) Davankov, V. A.; Bochkov, A. S.; Kurganov, A. A. *Chromatographia* **1980**, *13*, 677.
(27) Impellizzeri, G.; Bonomo, R. P.; Calì, R.; Cucinotta, V.; Rizzarelli, E. *Thermochim. Acta* **1984**, *72*, 263.
(28) Impellizeri, G.; Bonomo, R. P.; Calì, R.; Cucinotta, V.; Rizzarelli, E. *Thermochim. Acta* **1984**, *80*, 275.
(29) Arena, G.; Calì, R.; Cucinotta, V.; Musumeci, S.; Rizzarelli, E.; Sammartano, S. *J. Chem. Soc., Dalton Trans.* **1983**, 1271.
(30) Arena, G.; Calì, R.; Cucinotta, V.; Musumeci, S.; Rizzarelli, E.; Sammartano, S. *Thermochim. Acta* **1984**, *74*, 77.
(31) Arena, G.; Calì, R.; Cucinotta, V.; Musumeci, S.; Rizzarelli, E.; Sammartano, S. *J. Chem. Soc., Dalton Trans.* **1984**, 1651.
(32) Bonomo, R. P.; Calì, R.; Cucinotta, V.; Impellizzeri, G.; Rizzarelli, E. *Inorg. Chem.* **1986**, *25*, 1641.

0020-1669/89/1328-3555$01.50/0

Table I. Thermodynamic Parameters of Proton Complex Formation of Malonates at 25 °C and I = 0.1 mol dm^{-3} [a]

equilibrium	log K	$-\Delta G°$, kcal/mol	$\Delta H°$, kcal/mol	$\Delta S°$, cal/(mol deg)
$H^+ + MAL^{2-} \rightleftharpoons HMAL^-$	5.25[b]	7.16	0.65[c]	26.3[c]
$H^+ + HMAL^- \rightleftharpoons H_2MAL$	2.62[b]	3.57	-0.53[c]	10.0[c]
$H^+ + MeMAL^{2-} \rightleftharpoons HMeMAL^-$	5.35 (1)	7.30 (1)	0.58 (4)	26.4 (1)
$H^+ + HMeMAL^- \rightleftharpoons H_2MeMAL$	2.89 (2)	3.94 (3)	0.04 (3)	13.3 (1)
$H^+ + IProMAL^{2-} \rightleftharpoons HIProMAL^-$	5.49[d]	7.49	1.40 (1)	29.81 (4)
$H^+ + HIProMAL^- \rightleftharpoons H_2IProMAL$	2.74[d]	3.75	0.18 (1)	13.18 (3)
$H^+ + ProMAL^{2-} \rightleftharpoons HProMAL^-$	5.42 (1)	7.39 (1)	0.94 (1)	27.93 (4)
$H^+ + HProMAL^- \rightleftharpoons H_2ProMAL$	2.77 (2)	3.78 (3)	0.25 (2)	13.52 (6)
$H^+ + IBuMAL^{2-} \rightleftharpoons HIBuMAL^-$	5.36 (1)	7.31 (1)	0.82 (2)	27.23 (6)
$H^+ + HIBuMAL^- \rightleftharpoons H_2IBuMAL$	2.87 (1)	3.91 (1)	0.37 (3)	14.35 (9)
$H^+ + BuMAL^{2-} \rightleftharpoons HBuMAL^-$	5.46 (1)	7.45 (1)	0.95 (3)	28.2 (1)
$H^+ + HBuMAL^- \rightleftharpoons H_2BuMAL$	2.81 (2)	3.83 (3)	0.14 (5)	13.3 (1)
$H^+ + DMeMAL^{2-} \rightleftharpoons HDMeMAL^-$	5.65 (1)	7.70 (1)	1.02 (1)	29.25 (4)
$H^+ + MDMeMAL^- \rightleftharpoons H_2DMeMAL$	2.93 (2)	4.00 (3)	-0.11 (2)	13.93 (6)
$H^+ + DProMAL^{2-} \rightleftharpoons HDProMAL^-$	7.13 (1)	9.72 (1)	0.81 (5)	35.3 (1)
$H^+ + HDProMal^- \rightleftharpoons H_2DProMAL$	1.85 (3)	2.52 (4)	0.55 (1)	10.3 (1)
$H^+ + DBuMAL^{2-} \rightleftharpoons HDBuMAL^-$	7.19[d]	9.81	0.69 (4)	35.2 (1)
$H^+ + HDBuMAL^- \rightleftharpoons H_2DBuMAL$	2.00[d]	2.73	0.73 (4)	11.6 (1)
$H^+ + CPRD^{2-} \rightleftharpoons HCPRD^-$	7.19[e]	9.81[e]	0.38[e]	31.6[e]
$H^+ + HCPRD^- \rightleftharpoons H_2CPRD$	1.63[e]	2.22[e]	0.31[e]	8.5[e]

[a] 3σ values given in partentheses. [b] Reference 38. [c] Reference 39. [d] Reference 36. [e] Reference 44.

interact. In zinc(II) ternary complexes[29-31] the $\Delta H°$ and $\Delta S°$ values were diagnostic of the presence of noncovalent interactions, while in the analogous copper(II) complexes[29-31] the thermodynamic data seemed to indicate their absence, thus suggesting that the geometric coordination requirements of the metal ion influenced such an interaction occurrence.

This paper deals with the ligand–ligand interactions in systems containing a metal ion, the 2,2′-bipyridyl ligand (bpy), and malonate ligands (L) in which the methylene hydrogen atoms are substituted with alkyl residues, so that different distances may be obtained between the alkyl chains of the coordinating carboxylate groups and the pyridine rings of the diimine bound to the metal ion. To have further information on these complexes, EPR and ^1H NMR parameters have also been determined, in addition to potentiometric and calorimetric measurements.

Experimental Section

Chemicals. 2,2′-Bipyridyl (Erba RPE) was recrystallized from a water–ethanol mixture. The pK value was in agreement with the value (pK = 4.461) previously determined.[33] Dicarboxylic acids were prepared by hydrolysis of the related diethyl esters (Fluka), and their purity (≥99.6%) was checked by both alkalimetric titrations and melting point determination. Metal nitrate stock solutions were prepared and standardized as previously reported.[29] Standard solutions were prepared by using twice-distilled water. 2,9-Dimethyl-1,10-phenanthroline (Fluka) was used as received.

EMF Measurements. Details of potentiometric measurements were previously described.[34-39] The electrode couple was standardized by titrating HNO_3 (5–10 mmol dm^{-3}) with KOH (100 mmol dm^{-3}) at 25 °C and I = 0.1 mol dm^{-3} (KNO_3). At least five independent potentiometric titrations have been performed for each system.

Calorimetric Measurements. Details of the calorimetric measurements are as previously reported.[29,40] The heats of protonation were obtained by titrating the malonic acids (15–60 mmol dm^{-3}) with 100 mmol dm^{-3} KOH and by titrating HL^-/L^{2-} buffers (10–20 mmol dm^{-3}) with HNO_3. The simple metal complex formation heats were determined by using either the dicarboxylate ligand or a solution containing the metal ion as titrants. The formation heats of mixed species were determined by titrating copper(II)– or zinc(II)–Bpy systems with malonate dianions. At least seven titrations for each system have been carried out. Throughout this paper the calorie unit is equivalent to 4.184 J.

EPR Spectra. EPR spectra were recorded with a conventional X-band spectrometer (Bruker ER 200 D) operating at 9.3–9.5 GHz, equipped with a standard low-temperature unit. Metal complex solutions were prepared in water by adding the appropriate mono- or disubstituted malonate to copper(II) nitrate and adjusting the pH to a value of about 6. A typical molar ratio for the mono species was $[Cu^{2+}]:[L]$ = 1.05:1, while that for the bis species was $[Cu^{2+}]:[L]$ = 1:10 ($[Cu^{2+}]$ = 5 mmol dm^{-3}). In the case of the mixed complexes a slight excess of malonate was employed (typical molar ratios were $[Cu^{2+}]:[bpy]:[L]$ = 1:1:2). Methanol up to 10% was added to these solutions to improve resolution. All the spectra were run at the temperature of 150 K.

^1H NMR Spectra. ^1H NMR spectra were obtained at 80 MHz with a Bruker WP-80 spectrometer in D_2O solution in the Fourier transform mode. The uncertainties in the chemical shift values were ±0.2 Hz. The dianion analytical concentrations were 1–5 mmol dm^{-3}. For each simple or mixed species, the respective $[Zn^{2+}]:[L]$ and $[Zn^{2+}]:[bpy]:[L]$ concentration ratios were chosen in order to optimize their formation degree. The simulations were performed by the computer program DOEC[41] using the previously determined formation constants. However, owing to the rather low values of formation constants, formation degrees ranging from 50% to 70%, depending on the specific system, were obtained together with significative percentages of both free mono- and dianion. DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid), the usual ^1H NMR reference in water, has not been used in order to prevent the eventual interference of the trimethylsilyl group with the intramolecular hydrophobic interaction. Thus, TMA (tetramethylammonium ion) was used throughout as reference (3.188 ppm).

Calculations. ACBA,[42] MINIQUAD,[43] and DOEC[41] programs were used to calculate the parameters of an acid–base titration, the formation constants, and the $\Delta H°$ values for the proton and the metal complex formation, respectively.

Throughout the paper the errors in the thermodynamic parameters are expressed as 3 times the standard deviation or uncertainty range (maximum deviation from the mean).

Results and Discussion

Influence of Side-Chain Groups on the Thermodynamic Parameters. Proton Complex Formation. The values of log K, $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the protonation of the malonate ligands are reported in Table I. Thermodynamic data for dicarboxylate ligand protonations in aqueous solution have been reported[44,45]

---

(33) Maggiore, R.; Musumeci, S.; Rizzarelli, E.; Sammartano, S. *Inorg. Chim. Acta* **1976**, *18*, 155.

(34) Ostacoli, G.; Vanni, A.; Roletto, E. *Ric. Sci.* **1968**, *38*, 318.

(35) Ostacoli, G.; Vanni, A.; Roletto, E. *Gazz. Chim. Ital.* **1970**, *100*, 350.

(36) Ostacoli, G.; Daniele, P. G.; Vanni, A. *Ann. Chim. (Rome)* **1973**, *63*, 815.

(37) Daniele, P. G.; Ostacoli, G.; Zelano, V. *Ann. Chim. (Rome)* **1975**, *65*, 617.

(38) Bonomo, R. P.; Musumeci, S.; Rizzarelli, E.; Sammartano, S. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1851.

(39) Arena, G.; Calì, R.; Rizzarelli, E.; Sammartano, S. *Transition Met. Chem.* **1978**, *3*, 147.

(40) Calì, R.; Rizzarelli, E.; Sammartano, S.; Pettit, L. D. *Thermochim. Acta* **1980**, *35*, 159.

(41) Rigano, C.; Rizzarelli, E.; Sammartano, S. *Thermochim. Acta* **1979**, *33*, 211.

(42) Arena, G.; Rizzarelli, E.; Sammartano, S.; Rigano, C. *Talanta* **1979**, *26*, 1.

(43) Gans, P.; Vacca, A.; Sabatini, A. *Inorg. Chim. Acta* **1976**, *18*, 237.

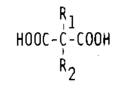
(44) Calì, R.; Gurrieri, S.; Rizzarelli, E.; Sammartano, S. *Thermochim. Acta* **1975**, *12*, 19.

Table II. Thermodynamic Functions of Copper(II) Simple Malonate Complexes at 25 °C and $I = 0.1$ mol dm^{-3}[a]

equilibrium	log K	$-\Delta G°$, kcal/mol	$\Delta H°$, kcal/mol	$\Delta S°$, cal/(mol deg)
$Cu^{2+} + MAL^{2-} \rightleftharpoons [Cu(MAL)]$	5.05[b]	6.88[b]	1.41[b]	27.7[b]
$[Cu(MAL)] + MAL^{2-} \rightleftharpoons [Cu(MAL)_2]^{2-}$	2.90[b]	3.90[b]	−0.19[b]	12.4[b]
$Cu^{2+} + MeMAL^{2-} \rightleftharpoons [Cu(MeMAL)]$	4.89[c]	6.67	2.17 (3)	29.6 (1)
$[Cu(MeMAL)] + MeMAL^{2-} \rightleftharpoons [Cu(MeMAL)_2]^{2-}$	2.60[c]	3.54	0.34 (6)	13.1 (2)
$Cu^{2+} + IProMAL^{2-} \rightleftharpoons [Cu(IProMAL)]$	5.37[d]	7.32	1.65 (3)	30.1 (3)
$[Cu(IProMAL)] + IProMAL^{2-} \rightleftharpoons [Cu(IProMAL)_2]^{2-}$	3.59[d]	4.89	0.52 (5)	18.1 (2)
$Cu^{2+} + ProMAL^{2-} \rightleftharpoons [Cu(ProMAL)]$	4.92 (1)	6.70 (1)	2.46 (3)	30.8 (1)
$[Cu(ProMAL)] + ProMAL^{2-} \rightleftharpoons [Cu(ProMAL)_2]^{2-}$	3.22 (2)	4.39 (3)	1.06 (6)	18.3 (2)
$Cu^{2+} + IBuMAL^{2-} \rightleftharpoons [Cu(IBuMAL)]$	4.84 (1)	6.60 (1)	2.48 (1)	30.45 (4)
$[Cu(IBuMAL)] + IBuMAL^{2-} \rightleftharpoons [Cu(IBuMAL)_2]^{2-}$	3.08 (2)	4.20 (3)	1.47 (4)	19.1 (2)
$Cu^{2+} + BuMAL^{2-} \rightleftharpoons [Cu(BuMAL)]$	4.98 (1)	6.79 (1)	2.43 (5)	30.9 (2)
$[Cu(BuMAL)] + BuMAL^{2-} \rightleftharpoons [Cu(BuMAL)_2]^{2-}$	3.34 (2)	4.55 (3)	1.26 (6)	19.5 (2)
$Cu^{2+} + DMeMAL^{2-} \rightleftharpoons [Cu(DMeMAL)]$	4.57[e]	6.23	3.93 (3)	34.1 (1)
$[Cu(DMeMAL)] + DMeMAL^{2-} \rightleftharpoons [Cu(DMeMAL)_2]^{2-}$	2.52[e]	3.44	1.96 (3)	18.1 (1)
$Cu^{2+} + DProMAL^{2-} \rightleftharpoons [Cu(DProMAL)]$	5.15 (1)	7.02 (1)	3.27 (6)	34.5 (2)
$[Cu(DProMAL)] + DProMAL^{2-} \rightleftharpoons [Cu(DProMAL)_2]^{2-}$	3.18 (2)	4.34 (3)	3.05 (9)	24.8 (4)
$Cu^{2+} + DBuMAL^{2-} \rightleftharpoons [Cu(DBuMAL)]$	5.10[e]	6.95	3.29 (5)	34.3 (2)
$[Cu(DBuMAL)] + DBuMAL^{2-} \rightleftharpoons [Cu(DBuMAL)_2]^{2-}$	3.05[e]	4.16	3.75 (8)	26.5 (3)

[a] 3σ values given in parentheses. [b] Reference 39. [c] Reference 34. [d] Reference 36. [e] Reference 35.

Chart I



$$HOOC-\overset{R_1}{\underset{R_2}{C}}-COOH$$

R_1	R_2	ABBREVIATION
-H	-H	MAL
-H	$-CH_3$	MeMAL
-H	$-CH_2-CH_3$	EtMAL
-H	$-CH_2-CH_2-CH_3$	ProMAL
-H	$-CH(CH_3)_2$	IProMAL
-H	$-CH_2-CH_2-CH_2-CH_3$	BuMAL
-H	$-CH_2-CH(CH_3)_2$	IBuMAL
-H	$-CH_2-C_6H_5$	BeMAL
$-CH_3$	$-CH_3$	DMeMAL
$-CH_2-CH_3$	$-CH_2-CH_3$	DEtMAL
$-CH_2-CH_2-CH_3$	$-CH_2-CH_2-CH_3$	DProMAL
$-CH_2-CH_2-CH_2-CH_3$	$-CH_2-CH_2-CH_2-CH_3$	DBuMAL

and the $\Delta H°$ and $\Delta S°$ values, as well as the pK differences (pK = log K_1 − log K_2), discussed on the basis of electrostatic theories (electrostatic interaction between carboxylate groups) and intramolecular hydrogen bonding in monoanions.[45,46]

As shown in Table I, an increasing spread of the two constants can be observed in the dialkylmalonates, especially for the dipropyl and dibutyl derivatives. The first protonation step of these two dianions shows a $\Delta S°$ value more positive than that for the dimethylmalonate as well as the other monoalkyl derivatives. To explain this trend, one has to consider that the two carboxylate groups will stay as far apart as possible in order to minimize their electrostatic interaction. The formation of the monoanion relieves this electrostatic repulsion to some extent. This protonation step is entropy-driven, due to the desolvation processes of the charged groups caused by the partial neutralization of the charges. The small differences among the monosubstituted malonates seem to reflect small structural differences due to the type of chain. The introduction into malonic acid of two large substituents restricts the possibility of free rotation of carboxylate groups, as one can see by the Dreiding models. The dianion will be destabilized, the carboxylate groups being forced closer to each other. At some critical separation, a hydrogen bond occurs in the monoanion, giving rise to an entropic stabilization. The same behavior is shown by cyclopropanedicarboxylic acid,[44] in which the rigid ring constrains the carboxylate groups in a coplanar situation (see Table I).

Simple Complex Formation. As previously reported for analogous copper(II) dicarboxylate complexes,[39,47,48] the formation reactions are endothermic and the entropy values are large and positive (see Table II). In the first step the exothermic formation of the new bonds is counterbalanced by both the more endothermic reaction of metal desolvation and the breakdown of the solvent lattice around the reacting species. On the other hand, the subsequent release of solvent molecules, due to neutralization of the cation charge, accounts for the positive entropy changes. The introduction of an alkyl group slightly decreases the stability of the copper(II) complexes with respect to that of [Cu(MAL)], except for [Cu(IProMAL)], which is the most stable. In the case of disubstituted dicarboxylates, the stability of [Cu(DProMAL)] and [Cu(DBuMAL)] complexes is larger than that of [Cu(MAL)] and [Cu(DMeMAL)] due to a less unfavored enthalpy contribution. As in the case of free dianion protonation results, the introduction of the substituent gives a certain amount of rigidity to the position of the coordinating groups, in DPro and DBu malonates, matching well with the peculiar geometry of the coordination sphere of the copper(II) ion. This explanation can be extended to the [Cu(IProMAL)] species, as well. In the case of IProMAL proton complexation this effect is less evident, even if the $\Delta S°_1$ value is the most positive among the monoalkyl derivatives.

The $\Delta H°$ and $\Delta S°$ changes due to the formation of bis complexes are lower than those obtained for the mono complexes (Table II). Formation of a doubly charged anionic complex from an uncharged complex involves less desolvation and, consequently, a less positive $\Delta H°$ value, as previously found for other dicarboxylate ligands.[39]

$\Delta G°$, $\Delta H°$, and $\Delta S°$ values for the formation of simple zinc(II) complexes are reported in Table III. These species are enthalpically unfavored but entropically favored, as already found for the analogous copper(II) complexes. The stability of [Zn(MAL)] is not significantly altered by the introduction of one alkyl group. Unlike the case for the copper(II) complexes, the formation of

---

(45) Christensen, J. J.; Izatt, R. M.; Hansen, L. D. *J. Am. Chem. Soc.* **1967**, *89*, 213 and references therein.

(46) Eberson, L.; Wädso, I. *Acta Chem. Scand.* **1963**, *17*, 1552.

(47) Arena, G.; Calì, R.; Rizzarelli, E.; Sammartano, S. *Thermochim. Acta* **1976**, *11*, 155.

(48) Anderegg, G. *Helv. Chim. Acta* **1963**, *46*, 2813.

Table III. Thermodynamic Functions of Zinc(II) Simple Malonate Complexes at 25 °C and $I = 0.1$ mol dm^{-3} [a]

equilibrium	log K	$-\Delta G°$, kcal/mol	$\Delta H°$, kcal/mol	$\Delta S°$, cal/(mol deg)
$Zn^{2+} + MAL^{2-} \rightleftharpoons [Zn(MAL)]$	2.85[b]	3.89	2.66 (4)	22.0 (1)
$Zn^{2+} + MeMAL^{2-} \rightleftharpoons [Zn(MeMAL)]$	2.64 (4)	3.60 (6)	3.06 (7)	22.3 (2)
$Zn^{2+} + HMeMAL^{-} \rightleftharpoons [Zn(HMeMAL)]^{+}$	1.05 (6)	1.43 (8)		
$[Zn(MeMAL)] + MeMAL^{2-} \rightleftharpoons [Zn(MeMAL)_2]^{2-}$	1.4 (1)	1.9 (1)		
$Zn^{2+} + IProMAL^{2-} \rightleftharpoons [Zn(IProMAL)]$	2.85 (3)	3.89 (4)	4.27 (7)	27.4 (2)
$[Zn(IProMAL)] + IProMAL^{2-} \rightleftharpoons [Zn(IProMAL)_2]^{2-}$	2.69 (4)	3.67 (5)		
$Zn^{2+} + ProMAL^{2-} \rightleftharpoons [Zn(ProMAL)]$	2.75 (4)	3.75 (6)	3.88 (4)	25.6 (1)
$Zn^{2+}\ HProMAL^{-} \rightleftharpoons [Zn(HProMAL)]^{+}$	1.15 (6)	1.57 (8)		
$[Zn(ProMAL)] + ProMAL^{2-} \rightleftharpoons |Zn(ProMAL)_2]^{2-}$	2.06 (6)	2.81 (8)		
$Zn^{2+} + IBuMAL^{2-} \rightleftharpoons [Zn(IBuMAL)]$	2.97 (3)	4.05 (4)	3.71 (6)	26.0 (2)
$Zn^{2+} + HIBuMAL^{-} \rightleftharpoons [Zn(HIBuMAL)]^{+}$	2.01 (6)	2.74 (8)		
$[Zn(IBuMAL)] + IBuMAL^{2-} \rightleftharpoons [Zn(IBuMAL)_2]^{2-}$	2.03 (5)	2.77 (7)		
$Zn^{2+} + BuMAL^{2-} \rightleftharpoons [Zn(BuMAL)]$	2.80 (3)	3.82 (4)	3.59 (6)	24.8 (2)
$Zn^{2+} + HBuMAL^{2-} \rightleftharpoons [Zn(HBuMAL)]^{+}$	1.65 (6)	2.25 (8)		
$[Zn(BuMAL)] + BuMAL^{2-} \rightleftharpoons [Zn(BuMAL)_2]^{2-}$	2.16 (5)	2.95 (7)		
$Zn^{2+} + DMeMAL^{2-} \rightleftharpoons [Zn(DMeMAL)]$	2.20[c]	3.00	4.48 (5)	25.0 (2)
$[Zn(DMeMAL)] + DMeMAL^{2-} \rightleftharpoons [Zn(DMeMAL)_2]^{2-}$	1.8 (1)	2.5 (2)		
$Zn^{2+} + DProMAL^{2-} \rightleftharpoons [Zn(DProMAL)]$	2.50 (2)	3.41 (3)	4.65 (5)	26.7 (2)
$[Zn(DProMAL)] + DProMAL^{2-} \rightleftharpoons [Zn(DProMAL)_2]^{2-}$	1.83 (5)	2.50 (7)		
$Zn^{2+} + DBuMAL^{2-} \rightleftharpoons [Zn(DBuMAL)]$	2.52 (3)	3.44 (4)	5.49 (6)	30.0 (2)
$[Zn(DBuMAL)] + DBuMAL^{2-} \rightleftharpoons [Zn(DBuMAL)_2]^{2-}$	1.99 (6)	2.71 (8)		

[a] 3σ values given in parentheses. [b] Reference 37. [c] Reference 34.

Table IV. Thermodynamic Functions of Copper(II) and Zinc(II) Simple Complexes with 2,2′-Bipyridyl at 25 °C and $I = 0.1$ mol dm^{-3} [a]

equilibrium	log K	$-\Delta G°$, kcal/mol	$-\Delta H°$, kcal/mol	$\Delta S°$, cal/(mol deg)
$Cu^{2+} + bpy \rightleftharpoons [Cu(bpy)]^{2+}$	8.11[b]	11.05	10.65[b]	1.3[b]
$[Cu(bpy)]^{2+} + bpy \rightleftharpoons [Cu(bpy)_2]^{2+}$	5.55[b]	7.57	6.09[b]	5.0[b]
$[Cu(bpy)_2]^{2+} + bpy \rightleftharpoons [Cu(bpy)_3]^{2+}$	3.39[b]	4.63	7.9[b]	-11.0[b]
$Zn^{2+} + bpy \rightleftharpoons [Zn(bpy)]^{2+}$	5.04[c]	6.87	7.04 (3)	-0.6 (1)
$[Zn(bpy)]^{2+} + bpy \rightleftharpoons [Zn(bpy)_2]^{2+}$	4.50[c]	6.14	6.06 (6)	0.3 (2)
$[Znnbpy)_2]^{2+} + bpy \rightleftharpoons [Zn(bpy)_3]^{2+}$	3.20[c]	4.36	5.38 (6)	-3.4 (2)

[a] 3σ values given in parentheses. [b] Reference 48. [c] Reference 37.

Table V. Thermodynamic Functions for the Formation of Copper(II) Mixed Complexes with Malonates and 2,2′-Bipyridyl at 25 °C and $I = 0.1$ mol dm^{-3} [a]

equilibrium	log β	$-\Delta G°$, kcal/mol	$-\Delta H°$, kcal/mol	$\Delta S°$, cal/(mol deg)
$Cu^{2+} + bpy + MAL^{2-} \rightleftharpoons [Cu(bpy)(MAL)]$	13.40[b]	18.28	10.21[b]	27.2[b]
$Cu^{2+} + bpy + MeMAL^{2-} \rightleftharpoons [Cu(bpy)(MeMAL)]$	13.32[c]	18.17	10.90 (2)	24.38 (6)
$Cu^{2+} + bpy + IProMAL^{2-} \rightleftharpoons [Cu(bpy)(IProMAL)]$	13.98[d]	19.07	10.42 (1)	29.01 (3)
$Cu^{2+} + bpy + ProMAL^{2-} \rightleftharpoons [Cu(bpy)(ProMAL)]$	13.40 (1)	18.28 (1)	10.24 (1)	26.97 (3)
$Cu^{2+} + bpy + IBuMAL^{2-} \rightleftharpoons [Cu(bpy)(IBuMAL)]$	13.42 (1)	18.30 (1)	9.81 (1)	28.48 (3)
$Cu^{2+} + bpy + BuMAL^{2-} \rightleftharpoons [Cu(bpy)(BuMAL)]$	13.30[c]	18.14 (1)	9.32 (1)	29.58 (3)
$Cu^{2+} + bpy + DMeMAL^{2-} \rightleftharpoons [Cu(bpy)(DMeMAL)]$	12.81[c]	17.47	7.98 (3)	31.83 (9)
$Cu^{2+} + bpy + DProMAL^{2-} \rightleftharpoons [Cu(bpy)(DProMAL)]$	13.81 (1)	18.83 (1)	8.80 (2)	33.64 (6)
$Cu^{2+} + bpy + DBuMAL^{2-} \rightleftharpoons [Cu(bpy)(DBuMAL)]$	13.72[d]	18.71	9.01 (4)	32.5 (1)

[a] 3σ values given in parentheses. [b] Reference 50. [c] Reference 38. [d] Reference 36.

the zinc(II) complexes with unsubstituted malonate and monoalkylmalonates is more favored than that with the dipropyl- and dibutylmalonates, which show the most unfavorable enthalpy contribution. Hence, the large substituents, forcing the carboxylate groups to stand closer and coplanar, favor the formation of the copper(II) complexes, while in the zinc(II) complexes this ligand structural feature does not contribute in a favorable way, probably owing to a preference for a tetrahedral stereochemistry by the zinc(II) ions. Moreover, the similarity among isopropyl, di-*n*-propyl, and di-*n*-butyl derivatives is reconfirmed.

Table IV shows the thermodynamic data pertinent to the complex formation of copper(II) and zinc(II) with 2,2′-bipyridyl.[37,48]

Mixed Complex Formation. The thermodynamic parameters concerning the formation of copper(II) ternary complexes show negative enthalpy and positive entropy changes (Table V), as found for other copper(II) mixed complexes with bpy and dicarboxylates.[49,50] The trend of stability is the same as that observed in the simple malonate complexes and can be ascribed to the same geometric features already discussed. In fact, [Cu(bpy)(IProMAL)] is the most stable complex along the series of the mixed complexes with the monoalkyl derivatives and [Cu(bpy)(DBuMAL)] and [Cu(bpy)(DProMAL)] are more stable than [Cu(bpy)(DMeMAL)].

$\Delta G°$, $\Delta H°$, and $\Delta S°$ values for the formation of zinc(II) mixed complexes are given in Table VI. From the $\Delta G°$ values only, the complexes seem to have a similar behavior. The zinc(II) complexation is both enthalpically and entropically favored. The negative enthalpy changes indicate that bipyridyl is acting as a bidentate ligand, while the positive entropy values are ascribable to the neutralization of the metal ion charge. [Zn(bpy)(BuMAL)] formation is more enthalpically and less entropically favored than for all the other ternary complexes. This behavior is also shown by [Zn(bpy)(DBuMAL)] and [Zn(bpy)(DProMAL)] if compared with [Zn(bpy)(DMeMAL)]. This trend is different from what is found for zinc(II) malonate simple complexes (Table III). In

---

(49) Arena, G.; Calì, R.; Rizzarelli, E.; Sammartano, S.; Barbucci, R.; Campbell, M. J. M. *J. Chem. Soc., Dalton Trans.* **1977**, 581.

(50) Arena, G.; Calì, R.; Rizzarelli, E.; Sammartano, S.; Barbucci, R.; Campbell, M. J. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1090.

Table VI. Thermodynamic Functions for the Formation of Zinc(II) Mixed Complexes with Malonates and 2,2′-Bipyridyl at 25 °C and I = 0.1 mol dm^{-3} [a]

equilibrium	log β	$-\Delta G°$, kcal/mol	$-\Delta H°$, kcal/mol	$\Delta S°$, cal/(mol deg)
Zn^{2+} + bpy + MAL^{2-} ⇌ [Zn(bpy)(MAL)]	7.95[b]	10.84	4.48 (7)	21.4 (3)
Zn^{2+} + bpy + $MeMAL^{2-}$ ⇌ [Zn(bpy)(MeMAL)]	7.64 (3)	10.42 (5)	3.63 (8)	22.8 (3)
Zn^{2+} + bpy + $IProMAL^{2-}$ ⇌ [Zn(bpy)(IProMAL)]	8.02 (4)	10.94 (6)	1.91 (6)	30.3 (2)
Zn^{2+} + bpy + $ProMAL^{2-}$ ⇌ [Zn(bpy)(ProMAL)]	7.52 (4)	10.25 (6)	3.70 (8)	22.0 (4)
Zn^{2+} + bpy + $IBuMAL^{2-}$ ⇌ [Zn(bpy)(IBuMAL)]	7.77 (4)	10.59 (6)	3.30 (9)	24.4 (3)
Zn^{2+} + bpy + $BuMAL^{2-}$ ⇌ [Zn(bpy)(BuMAL)]	7.83 (4)	10.68 (6)	8.77 (9)	6.4 (4)
Zn^{2+} + bpy + $DMeMAL^{2-}$ ⇌ [Zn(bpy)(DMeMAL)]	7.30 (3)	9.96 (4)	1.97 (9)	26.8 (4)
Zn^{2+} + bpy + $DProMAL^{2-}$ ⇌ [Zn(bpy)(DProMAL)]	7.65 (4)	10.43 (6)	3.81 (9)	22.2 (4)
Zn^{2+} + bpy + $DBuMAL^{2-}$ ⇌ [Zn(bpy)(DBuMAL)]	8.25 (3)	11.25 (4)	3.62 (2)	25.6 (4)

[a] 3σ values given in parentheses. [b] Reference 36.

Table VII. Thermodynamic Functions of the 2,2′-Bipyridyl Coordination to Zinc(II) and Copper(II) Malonate Complexes at 25 °C and I = 0.1 mol dm^{-3}

equilibrium	log β	$-\Delta G°$, kcal/mol	$-\Delta H°$, kcal/mol	$\Delta S°$, cal/(mol deg)
[Zn(MAL)] + bpy ⇌ [Zn(bpy)(MAL)]	5.10	6.95	7.14	−0.6
Zn(MeMAL)] + bpy ⇌ [Zn(bpy)(MeMAL)]	5.00	6.82	6.69	0.5
[Zn(IProMAL)] + bpy ⇌ [Zn(bpy)(IProMAL)]	5.17	7.05	6.18	2.9
[Zn(ProMAL)] + bpy ⇌ [Zn(bpy)(ProMAl)]	4.77	6.50	7.58	−3.6
[ZnnIBuMAL)] + bpy ⇌ [Zn(bpy)(IBu/MAL)]	4.80	6.54	7.01	−1.6
[Zn(BuMAL)] + bpy ⇌ [Zn(bpy)(BuMAL)]	5.03	6.86	12.36	−18.4
[Zn(DMeMAL)] + bpy ⇌ [Zn(bpy)(DMeMAL)]	5.10	6.96	6.45	1.8
[Zn(DProMAL)] + bpy ⇌ [Zn(bpy)(DProMAL)]	5.15	7.02	8.46	−4.5
[Zn(DBuMAL)] + bpy ⇌ [Zn(bpy)(DBuMAL)]	5.73	7.81	9.10	−4.4
[Cu(MAL)] + bpy ⇌ [Cu(bpy)(MAL)]	8.35	11.40	11.62	−0.5
[Cu(MeMAL)] + bpy ⇌ [Cu(bpy)(MemAL)]	8.43	11.50	13.07	−5.6
[Cu(IProMAL)] + bpy ⇌ [Cu(bpy)(IProMAL)]	8.61	11.75	12.07	−1.0
[Cu(ProMAL)] + bpy ⇌ [Cu(bpy)(ProMAL)]	8.48	11.57	12.70	−3.6
[Cu(IBuMAL)] + bpy ⇌ [Cu(bpy)(IBuMAL)]	8.58	11.70	12.29	−2.1
[Cu(BuMAL)] + bpy ⇌ [Cu(bpy)(BuMAL)]	8.32	11.35	11.75	−1.3
[Cu(DMeMAL)] + bpy ⇌ [Cu(bpy)(DMeMAL)]	8.24	11.24	11.91	−2.3
[Cu(DProMAL)] + bpy ⇌ [Cu(bpy)(DProMAL)]	8.66	11.81	12.07	−0.9
[Cu(DBuMAL)] + bpy ⇌ [Cu(bpy)(DBuMAL)]	8.62	11.76	12.30	−1.8

fact, in the binary systems the presence of a long chain involves an enthalpy contribution that is more positive than that found for both unsubstituted malonate and short-side-chain mono- and disubstituted malonates.

Recently, the enhanced stability of mixed copper(II) and zinc(II) complexes with monocarboxylate anions (L) containing alkyl or aryl substituent groups and 1,10-phenanthroline or 2,2′-bipyridyl (L′) was attributed to a solvophobic[51] or, according to a more classic definition, hydrophobic[52] and stacking[53] ligand–ligand interactions, on the basis of the relationship between log K^{M}_{ML} or log $K^{ML'}_{ML'L}$ and pK^{H}_{HL}.[54-57] For our systems, the plot of log K^{M}_{ML} vs pK^{H}_{HL} + $pK^{HL}_{H_2L}$ does not reveal any simple relationship between the stability of the binary complexes and the basicity of the ligands. Hence, the carboxylate dianions, though having the same donor atoms, cannot be considered as belonging to one series of structurally simple related ligands.[58] No comparison with the corresponding relationship of ternary complexes can be made. However, the values of thermodynamic parameters pertinent to the equilibrium [Zn(L)] + bpy ⇌ [Zn(bpy)(L)] can be more useful (Table VII). In fact, assuming as reference systems the complexes with MeMAL and DMeMAL derivatives for the mono- and disubstituted malonates, respectively, the favorable enthalpy contribution to the complex formation increases with the increase in length and in size of alkyl residues starting from the *n*-propyl group, while the entropy changes go from positive to negative values. The behavior of mixed zinc(II) complexes can be rationalized by assuming that a solvophobic interaction between the alkyl residues and the pyridyl rings is present in both the complexes of monosubstituted (R_1 = *n*-propyl, isobutyl, and *n*-butyl) and disubstituted (R_1 = R_2 = *n*-propyl and *n*-butyl) malonates. The presence of noncovalent interactions in metal complexes with biofunctional ligands previously showed an enthalpically favorable and an entropically unfavorable contribution.[29-31]

Table VIII. Spin Hamiltonian Parameters Obtained for Simple 1:2 Copper(II) Mono- and Disubstituted Malonate Complexes in Water–Methanol Mixtures at 150 K[a]

ligand	$g_{\parallel}$	$A_{\parallel}$, cm^{-1}	$g_{\perp}$	$A_{\perp}$, cm^{-1}
MAL	2.347	0.0162	2.076	0.0016
MeMAL	2.334	0.0167	2.074	0.0017
EtMAL	2.327	0.0169	2.070	0.0017
ProMAL	2.326	0.0169	2.069	0.0016
BuMAL	2.325	0.0169	2.069	0.0017
IProMAL	2.324	0.0169	2.069	0.0017
IBuMAL	2.325	0.0170	2.069	0.0016
IPenMAL	2.324	0.0170	2.069	0.0016
BenMAL	2.321	0.0168	2.069	0.0017
DMeMAL	2.319	0.0173	2.067	0.0015
DEtMAL	2.320	0.0172	2.067	0.0016
DProMAL	2.319	0.0172	2.069	0.0015
DBuMAL	2.319	0.0173	2.068	0.0016

[a] Errors: $g_{\parallel}$ = 0.002; $A_{\parallel}$ = 0.0002 cm^{-1}; $g_{\perp}$ = 0.005; $A_{\perp}$ = 0.0004 cm^{-1}.

The thermodynamic functions associated with the formation of mixed copper(II) complexes (see Table VII) do not show an

---

(51) Sinanoglu, O. In *Molecular Interaction*; Ratajczak, H., Orville-Thomas, W. J., Eds.; Wiley: New York, 1982; Vol. 3, p 283.

(52) Ben-Naim, A. *Hydrophobic Interaction*; Plenum Press: New York, 1980.

(53) *Molecular Association in Biology*; Pulman, B., Ed.; Academic Press: New York, 1968. Porschke, D.; Eggers, F. *Eur. J. Biochem.* **1972**, *26*, 490.

(54) Sigel, H. *Angew. Chem.* **1982**, *94*, 421; *Angew. Chem., Int. Ed. Engl.* **1982**, 389.

(55) Dubler, E.; Haring, U. K.; Scheller, K. H.; Baltzer, P.; Sigel, H. *Inorg. Chem.* **1984**, *23*, 3785.

(56) Malini-Balakrishnan, R.; Scheller, K. H.; Haring, U. K.; Tribolet, R.; Sigel, H. *Inorg. Chem.* **1985**, *24*, 2067.

(57) Sigel, H.; Tribolet, R.; Scheller, K. H. *Inorg. Chim. Acta* **1985**, *100*, 151.

(58) Martell, A. E.; Calvin, M. *Chemistry of the Metal Chelate Compounds*; Prentice-Hall: Englewood Cliffs, NJ, 1952.

Table IX. Spin Hamiltonian Parameters Obtained for Copper(II) Mono- or Disubstituted Malonate Mixed Complexes with 2,2′-Bipyridyl in Water–Methanol Mixtures at 150 K[a]

ligand	$g_\parallel$	$A_\parallel$, cm^{-1}	$g_\perp$	$A_\perp$, cm^{-1}	$A^N{}_\perp$, cm^{-1}
MAL	2.268	0.0185	2.055	0.0013	0.0012
MeMAL	2.266	0.0186	2.054	0.0012	0.0012
EtMAL	2.267	0.0186	2.055	0.0012	0.0013
ProMAL	2.266	0.0186	2.055	0.0012	0.0013
BuMAL	2.267	0.0186	2.055	0.0012	0.0013
IProMAL	2.266	0.0187	2.057	0.0013	0.0013
IBuMAL	2.268	0.0186	2.058	0.0012	0.0013
IPenMAL	2.268	0.0186	2.054	0.0013	0.0013
BenMAL	2.260	0.0189	2.053	0.0014	0.0013
DMeMAL	2.260	0.0190	2.056	0.0012	0.0013
DEtMAL	2.264	0.0188	2.055	0.0013	0.0013
DProMAL	2.264	0.0189	2.057	0.0012	0.0013
DBuMAL	2.264	0.0188	2.056	0.0012	0.0013

[a] Errors: $g_\parallel$ = 0.02; $A_\parallel$ = 0.002 cm^{-1}; $g_\perp$ = 0.005; $A_\perp$ = 0.0004 cm^{-1}; A^N = 0.0002 cm^{-1}. The $A^N{}_\parallel$ values for all complexes is 0.0010 cm^{-1}.

analogous trend, and one could assert that the noncovalent interactions are not present, unless a change in the species coordination number occurs along the series. In fact, a further desolvation of the metal ion would be accompanied by an enthalpically unfavorable and an entropically favorable contribution, thus masking the thermodynamic effect due to a possible solvophobic interaction. Therefore, the presence of noncovalent interactions in the mixed copper(II) complexes could be excluded only if the coordination number of the metal ion is proved to be the same.

EPR Parameters and Coordination Geometric Features of Copper(II) Complexes. Tables VIII and IX collect the magnetic parameters associated with the bis species and the ternary complexes with 2,2′-bipyridyl. With regard to the values for the mono species, the values of the magnetic parameters are nearly the same, showing no dependence on the type of substituent ($\bar{g}_\parallel$ = 2.355 ± 0.001, $\bar{A}_\parallel$ = 0.0162 ± 0.0001 cm^{-1}, $\bar{g}_\perp$ = 2.081 ± 0.001, $\bar{A}_\perp$ = 0.0013 ± 0.0001 cm^{-1}), except for those of IProMAL ($g_\parallel$ = 2.346, $A_\parallel$ = 0.0164 cm^{-1}) and to a lesser extent for DProMAL ($g_\parallel$ = 2.352, $A_\parallel$ = 0.0164 cm^{-1}) and DBuMAL ($g_\parallel$ = 2.351, $A_\parallel$ = 0.0164 cm^{-1}). These data suggest that the complexes achieve the same pseudooctahedral stereochemistry,[59] the slight differences observed in the case of IProMAL, DProMAL, and DBuMAL being ascribable to geometrical factors caused by the presence of bulky substituents.

In the case of the bis species (see Table VIII) there is a marked decrease in $g_\parallel$ values and a moderate increase in $A_\parallel$ values on going from MAL to MeMAL and EtMAL. As one goes along the series, the $g_\parallel$ value remains constant and, within a slight fluctuation, the $A_\parallel$ value as well. A slightly pronounced shift in both $g_\parallel$ and $A_\parallel$ can be observed for the disubstituted malonates. It is important to bear in mind that the bis species are negatively charged complexes. Thus, the lower $g_\parallel$ and higher $A_\parallel$ values found for the bis species respect the theoretically expected trend.[59] In this case, the electron-donating properties of the substituents are clearly evident.

In the case of the ternary complexes with 2,2′-bipyridyl (see Table IX) the magnetic parameters reflect the presence of the heterocyclic base in the coordination sphere of the copper(II) complexes. No substantial difference can be observed along the series, thus meaning that the presence of 2,2′-bipyridyl gives rise to a leveling effect, as already found in the case of other mixed complexes.[60] Superhyperfine splitting can be observed in the lowest field feature in the EPR spectra of these copper(II) complexes, as well as in the perpendicular region. Five lines can be easily seen on the lowest field parallel line, thus indicating that both nitrogen donor atoms belonging to 2,2′-bipyridyl are surely involved in the coordination with copper(II) ions. The magnetic parameters are characteristic of a CuN_2O_2 chromophore in a strong tetragonally distorted octahedral field,[59] the two apical solvent molecules being surely confined to longer distances.

Table X. Chemical Shifts (ppm) Downfield from DSS of Terminal Methyls of Alkyl Chains of Malonates in Zinc(II) Binary and 2,2′-Bipyridyl Ternary Systems Compared with the Values of the Free Dianions

ligand	free dianion	syst binary	syst ternary
MeMAL	1.232	1.342	1.255
ProMAL	1.094	1.138	1.075
IProMAL	1.079	1.174	1.166
BuMAL	0.877	0.880	0.793
IBuMAL	1.092	1.121	1.064
DMeMAL	1.246	1.306	1.300
DProMAL	1.076	1.114	0.827
DBuMAL	0.863	0.861	0.849

For a comparison with the pattern found for the ternary complexes containing 2,2′-bipyridyl, EPR spectra of the ternary complexes with 2,9-dimethyl-1,10-phenanthroline have also been run. Previous EPR studies on copper(II) chelates with the general formula $Cu(N\text{-}N)(CH_3COO)_2$, where N-N is 2,2′-bipyridyl or 2,9-dimethyl-1,10-phenanthroline, have shown differences in the magnetic parameters that are those one would expect by varying the stereochemistry from a pseudooctahedron with a flat equatorial plane to a pseudooctahedron with a tetrahedrally distorted equatorial plane.[61,62] Also in this case, along this series of copper(II) mixed complexes, the magnetic parameters ($\bar{g}_\parallel$ = 2.317 ± 0.002, $\bar{A}_\parallel$ = 0.0158 ± 0.0002 cm^{-1}, $\bar{g}_\perp$ = 2.061 ± 0.002, $\bar{A}_\perp$ = 0.0013 ± 0.0002 cm^{-1}) do not show substantial differences on varying the malonate dianions.

To conclude the discussion of the EPR results, the following points can be summed up: (a) Pseudooctahedral stereochemistries are obtained for all the complexes. (b) In the case of the mono complexes no effect of alkyl substituents can be noted, except for some subtle but reproducible difference in those with IProMAL, DProMAL, and DBuMAL dianions. (c) In the case of the bis complexes, which are negatively charged, a strong influence on the EPR parameters can be seen on varying the electronic ability of alkyl residues. (d) In the ternary species both 2,2′-bipyridyl and 2,9-dimethyl-1,10-phenanthroline have a leveling effect; though the latter causes the coordination plane to be slightly distorted toward a tetrahedral situation, no significant difference is observed along the series.

Some of our EPR results[32] on copper(II) complexes with diastereoisomeric dipeptides have shown that, in the presence of a solvophobic ligand–ligand interaction, little difference in the $g_\parallel$ and $A_\parallel$ parameters could be observed, the copper(II) chromophores being equal. No difference of this kind is observed in this case for the copper(II) mixed complexes with either 2,2′-bipyridine or 2,9-dimethyl-1,10-phenanthroline, thus giving no indication of the presence of an intramolecular ligand–ligand solvophobic interaction.

^{1}H NMR Investigation and the Solvophobic Interaction in Zinc(II) Complexes. ^{1}H NMR data are summarized in Table X. As is known, both protonation and metal complexation, involving electron donation by the ligand, are accompanied by a downfield shift. This behavior is shown by the data (Table X) referring to binary zinc(II) complexes. In contrast, when the data of the free dianion are compared with those of the ternary complexes, two different behaviors are observed. In the case of short side chains, a downfield shift of the methyl groups is shown also in these ternary complexes, similar to the case of the binary complexes. If we look at the chemical shifts of the terminal methyl groups of the ligands with longer side chains, an upfield shift is observed. Such behavior is found when the involved hydrogen atoms lie above or below an aromatic ring.[63] In our systems, it should be supposed that the peaks shift upfield as a consequence

---

(59) Peisach, J.; Blumberg, W. E. *Arch. Biochem. Biophys.* **1974**, *165*, 691.
(60) Rizzarelli, E. *Gazz. Chim. Ital.* **1982**, *112*, 139.
(61) Yokoi, H.; Addison, W. *Inorg. Chem.* **1977**, *16*, 1341.
(62) Rehorek, T. D.; Spindler, H. *Z. Anorg. Allg. Chem.* **1973**, *175*, 399.
(63) Wagner, K. G.; Lawaczeck, R. *J. Magn. Reson.* **1972**, *8*, 164.

of the methyl group proximity to the heteroaromatic system of bpy, this proximity being due to the solvophobic interaction.[55]

Comparison of the data in Table VII with those in Table X shows that the ternary complexes in which ^1H NMR data suggest the presence of solvophobic interaction are those whose formation is enthalpically favored and entropically unfavored. However, it should be emphasized that, in these systems, no quantitative estimation of the extent of solvophobic interaction may be made by comparing the upfield shift values for two distinct reasons. First of all, the spectrum is always the weighted mean of the contributions due to the different labile species of the observed ligand. In particular, in order to obtain acceptable percentages of the ternary complex, it is necessary to increase the zinc(II) ion concentration and, consequently, in order to avoid the hydroxide precipitation, it is necessary to slightly lower the pH, thus favoring the monoanion formation. In such species, the methyl is shifted downfield, contributing to a decrease in the upfield shift due to the intramolecular solvophobic interaction.

Second, if we also neglect the speculation on the open-form–closed-form equilibrium,[51] the upfield shift is a complex function of the electronic and geometric factors occurring in the specific system.

Concluding Remarks

Both thermodynamic parameters and the ^1H NMR data show that in the ternary zinc(II) complexes a solvophobic interaction occurs between the diimine heteroaromatic system and an alkyl side chain of the mono- or disubstituted malonate, provided that the side chain is long enough (at least three carbon atoms), as we have already noted in the stereoselective protonation of linear dipeptides.[64]

Usually, the stability data of ternary complexes, through the use of $\Delta \log K$ (the constant for the equilibrium $MA + MB \rightleftharpoons MAB + M$), have been correlated with the upfield shifts observed for the hydrogen atoms involved in the interaction.[65] However, in the case of copper(II) complexes, owing to the broadness of the ^1H NMR peaks caused by the copper(II)-promoted paramagnetic nuclear relaxation, the occurrence of intramolecular interactions between side chains has been also inferred by comparing the $\Delta \log K$ values with those of the mixed complexes, in which the length of the side chain prevents an intramolecular interaction.[54-57] Also our ternary copper(II) complexes have $\Delta \log K$ values higher than that of the ternary malonate one, but the ΔH° and ΔS° values, diagnostic in the case of zinc(II) complexes, show no occurrence of noncovalent interaction. An accidental masking effect, due to a different copper(II)–solvent interaction in the ternary complexes, can be excluded on the basis of the EPR data. Furthermore, the EPR data are in agreement with the thermodynamic data, especially in the cases of copper(II) IProMAL, DProMAL, and DBuMAL complexes. Even in the slightly tetrahedrally distorted complexes of the substituted phenanthroline, the different length and size of the alkyl chains do not give rise to significant differences in the EPR parameters. Thus, in these systems for the occurrence of intramolecular solvophobic interaction, a typical tetrahedral coordination geometry must be reached.

Acknowledgment. We thank the Ministry of Education (Rome, Italy) and CRRNSM (Palermo, Italy) for partial support of this work.

Registry No. MeMAL, 516-05-2; ProMAL, 616-62-6; IProMAL, 601-79-6; BuMAL, 534-59-8; IBuMAL, 4361-06-2; DMeMAL, 595-46-0; DProMAL, 1636-27-7; DBuMAL, 2283-16-1.

---

(64) Calì, R.; Cucinotta, V.; Impellizzeri, G.; Maugeri, M. C.; Rizzarelli, E. *Int. J. Pept. Protein Res.* **1988**, *32*, 262.

(65) Chauduri, P.; Sigel, H. *J. Am. Chem. Soc.* **1977**, *99*, 3142.

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305, and Department of Inorganic Chemistry, The University of Sydney, Sydney, NSW 2006, Australia

Reactions of Hexachloroosmate(IV) with Hydrazine Hydrate: Syntheses and Properties of Pentaammine(dinitrogen)osmium(II) Chloride and Decaammine(μ-nitrido)diosmium(IV) Chloride

Peter A. Lay[*,†] and Henry Taube[*,‡]

Received January 23, 1989

Slow addition of powdered $(NH_4)_2[OsCl_6]$ to $NH_2NH_2\cdot H_2O$, followed by refluxing for 10 h, results in a mixture of $[Os(NH_3)_5(N_2)]Cl_2$ and *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$. Further reaction of the mixture with $NH_2NH_2\cdot H_2O$ results in $\sim$90% yield of $[Os(NH_3)_5(N_2)]Cl_2$. When the reverse addition is performed (i.e. $NH_2NH_2\cdot H_2O$ is added to $(NH_4)_2[OsCl_6]$), the very exothermic reaction that follows produces the previously unknown nitrido-bridged complex $[(NH_3)_5OsNOs(NH_3)_5]Cl_5\cdot H_2O$ in $\sim$90% yield. This compound is a convenient starting material for the preparation of a variety of *trans,trans*-$[X(NH_3)_4OsNOs(NH_3)_4X]^{n+}$ complexes in high yields. The electronic absorption spectrum of $[(NH_3)_5OsNOs(NH_3)_5]Cl_5\cdot H_2O$ has been assigned with the aid of a MO diagram and a comparison of its spectrum with those of other μ-N^{3-} complexes of Ru and Os.

Introduction

Allen and co-workers first described the reaction of $NH_2NH_2\cdot H_2O$ with $(NH_4)_2[OsCl_6]$ under conditions that result in moderate to good yields of $[Os(NH_3)_5(N_2)]Cl_2$.[1,2] Because the dinitrogen complex is the starting material for the synthesis of a variety of pentaammine[3-12] and tetraammine[13-17] complexes, the reaction has been improved on by various workers.[3-5] In the same spirit, we have examined the reaction in more detail and also describe the results of the reverse addition of $NH_2NH_2\cdot H_2O$

[†] The University of Sydney.

[‡] Stanford University.

(1) Allen, A. D.; Stevens, J. R. *J. Chem. Soc., Chem. Commun.* **1967**, 1147.

(2) Allen, A. D.; Stevens, J. R. *Can. J. Chem.* **1972**, *50*, 3093–3099.

(3) Elson, C. M.; Gulens, J.; Page, J. A. *Can. J. Chem.* **1971**, *49*, 207–210.

(4) Bottomley, F.; Tong, S.-B. *Inorg. Synth.* **1976**, *16*, 9–13.

(5) Buhr, J. D.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2208–2212.

(6) Sen, J. P.; Taube, H. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 125–135.

(7) Allen, A. D.; Stevens, J. R. *Can. J. Chem.* **1973**, *51*, 92–98.

(8) Lay, P. A.; Magnuson, R. H.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658–7659.

0020-1669/89/1328-3561$01.50/0