

Note

The use of solvatochromic mixed copper(II) chelates with *N,N,N',N'*-tetramethylethylenediamine and tropolonato or hinokitiolato ligands, $[\text{Cu}(\text{trop}/\text{hino})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$, as indicator for Lewis basicity of solvents and low-coordinating anions

Aurore Camard ^a, Yoshinori Ihara ^b, Fumiko Murata ^c, Kurt Mereiter ^d,
Yutaka Fukuda ^c, Wolfgang Linert ^{a,*}

^a Institute of Applied Synthetic Chemistry, Vienna University of Technology, Vienna, Getreidemarkt 9/163-AC, A-1060-Vienna, Austria

^b Department of Chemistry, Faculty of Education, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan

^c Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112-8610, Japan

^d Institute of Chemical Technologies and Analytics, Vienna University of Technology, Vienna, Getreidemarkt 9/164, A-1060-Vienna, Austria

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Abstract

Mixed copper(II) chelates, $[\text{Cu}(\text{trop}/\text{hino})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$, were prepared with a tropolonato or hinokitiolato ligands (trop/hino) and *N,N,N',N'*-tetramethylethylenediamine (tmen). These chelates were, as expected, quite similar to the corresponding acetylacetonato analog $[\text{Cu}(\text{acac})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$, being fairly soluble in a large number of solvents and remarkably solvatochromic in them. They were also useful as excellent Lewis basicity indicators in solution because their d–d bands continuously shift to red in wider ranges with increasing DN (donor number) of solvent. The examination on addition of various anions to these solvatochromic systems led to a quantitative view of the competition between solvent molecule and anion for coordination to metal center.

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1. Introduction

A number of empirical scales for solvent polarity, mainly based upon effects of selected solvation process, have been proposed in order to systematize and correlate observed solvation effects, although only a few have gained widespread use [1]. The methods using solvatochromic behavior of transition metal complexes will also serve as visualized models of solute–solvent interactions.

Solvatochromism of metal complexes can be divided into two types [2–4]; the first type comprises the case where the color changes are brought about by the direct attachment of solvent molecules onto metal center, and the second type is due to the attachment of solvent molecules onto ligands. Among the former whose color changes are due to those of d–d transitions, copper(II) complexes with a strong Jahn–Teller effect can be anticipated to show simple and regular changes in their electronic spectra according to the strength of interactions with solvent molecules at the axial sites.

We have indicated that $[\text{Cu}(\text{acac})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ (acac = acetylacetonate, tmen = *N,N,N',N'*-tetramethylethylenediamine), well-known to be one of the

* Corresponding author. Tel.: +4315880115350; fax: +4315880116299.

E-mail address: wlinert@mail.zserv.tuwien.ac.at (W. Linert).

representative solvatochromic chelates, could be used as an excellent Lewis basicity indicator in solution due to its continuous shift of the absorption maxima while varying the Lewis basicity of the solvent [5,6]. In a continuation of this study, we show here that the new chelates containing tropolone(trop) or hinokitiol(hino) instead of acac, $[\text{Cu}(\text{trop}/\text{hino})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$, are more sensitive to changes in the donor properties of solvents than the acac analog, and become good models for estimating a quantitative view of competition between solvent molecule and anion for coordination to Cu(II) ion, when various anions were added in their solvatochromic systems.

2. Experimental

2.1. Materials

The mixed copper(II) chelates were prepared as follows. Copper(II) chloride dihydrate (2 mmol) is dissolved in methanol (5 cm³), and a methanolic solution (5 cm³) containing *N,N,N',N'*-tetramethylethylenediamine (tmen) and tropolone (trop) or hinokitiol (hino) is added with stirring. Then, sodium carbonate (1 mmol) is added to the solution, which is gently heated for 1 h and then filtered. The crude crystals obtained upon addition of sodium tetraphenylborate (3 mmol) to the filtrate are recrystallized from 1,2-dichloroethane. The brown-violet crystals obtained are kept over phosphorus(V) oxide overnight to dry up. Elemental analyses of the chelates gave the following data. *Anal. Calc.* for $[\text{Cu}(\text{trop})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$: C, 68.8; H, 6.7; N, 4.5. Found: C, 69.1; H, 6.4; N, 4.3%. *Anal. Calc.* for $[\text{Cu}(\text{hino})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$: C, 72.6; H, 7.2; N, 4.2. Found: C, 72.5; H, 7.0; N, 4.2%.

2.2. Spectral measurements

Electronic spectra of the chelates were recorded at room temperature with either a one-cell WPI Fiber optic UV–Vis spectrophotometer or a two-cell Varian Cary 17D UV–Vis spectrophotometer within the range of 250–780 nm using 1,2-dichloroethane as reference. The sample solutions were prepared by mixing 2 ml of 1,2-dichloroethane solution of the chelate (5 mM) and 1 ml of donor solvent; the measurements were carried out in such mixed solvent systems. In the case of the measurements in the presence of anions, the sample solutions were prepared by mixing 1 ml of 1,2-dichloroethane solution of the chelate (5 mM), 0.5 ml of 1,2-dichloroethane solution containing the anion A[−] (5 mM), and 0.5 ml of donor solvent. Recrystallized tetrabutylammonium salts were used as a source of anion supply, except for the acetate and carbonate for which ammonium salts were used.

2.3. X-ray crystallography

Single crystals of $[\text{Cu}(\text{trop})(\text{tmen})(\text{dce})]\text{B}(\text{C}_6\text{H}_5)_4$ (dce = 1,2-dichloroethane) and $[\text{Cu}(\text{trop})(\text{tmen})(\text{ac})]\text{B}(\text{C}_6\text{H}_5)_4$ (ac = acetone) were obtained by slow diffusion of diethyl ether in 1,2-dichloroethane and acetone solutions of $[\text{Cu}(\text{trop})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$. X-ray data were collected with a Bruker AXS Smart APEX CCD diffractometer and graphite monochromatized Mo K α radiation; $\lambda = 0.71073 \text{ \AA}$. Corrections for absorption were carried out with multi-scan method and SADABS program, structure solution with direct methods, structure refinement on F^2 with anisotropic displacement parameters for non-hydrogen atoms; hydrogen atoms were included in idealized positions (Bruker AXS, 2001: programs SMART, version 5.626; SAINT, version 6.36A; SADABS version 2.05; XPREP, version 6.12; SHELXTL, version 6.10. Bruker AXS Inc., Madison, WI, USA).

Crystal data for $[\text{Cu}(\text{trop})(\text{tmen})(\text{dce})]\text{B}(\text{C}_6\text{H}_5)_4$: $\text{C}_{39}\text{H}_{45}\text{BCl}_2\text{CuN}_2\text{O}_2$, $M = 719.02$, monoclinic, space group $P2_1/n$, $a = 18.597(3)$, $b = 9.241(2)$, $c = 21.650(4)$ Å, $\beta = 98.318(4)^\circ$, $V = 3681.4(12)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.297 \text{ g/cm}^3$, $T = 123(2) \text{ K}$, $\mu = 0.774 \text{ mm}^{-1}$, $F(000) = 1508$, violet prism ($0.65 \times 0.28 \times 0.20 \text{ mm}$), total/unique reflections 26783/10374, $R_{\text{int}} = 0.022$, $\theta_{\text{max}} = 30^\circ$; final refinement: data/restraints/parameters 10374/0/425, GOF = 1.02, $R_1(wR_2) = 0.032$ (0.079) ($I > 2\sigma(I)$).

Crystal data for $[\text{Cu}(\text{trop})(\text{tmen})(\text{ac})]\text{B}(\text{C}_6\text{H}_5)_4$: $\text{C}_{40}\text{H}_{47}\text{BCuN}_2\text{O}_3$, $M = 678.15$, monoclinic, space group $P2_1/n$, $a = 10.0011(17)$, $b = 21.466(4)$, $c = 17.074(3)$ Å, $\beta = 94.590(3)^\circ$, $V = 3653.8(11)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.233 \text{ g/cm}^3$, $T = 297(2) \text{ K}$, $\mu = 0.636 \text{ mm}^{-1}$, $F(000) = 1436$, violet prism ($0.75 \times 0.28 \times 0.27 \text{ mm}$), total/unique reflections 43191/7934, $R_{\text{int}} = 0.029$, $\theta_{\text{max}} = 27^\circ$; final refinement: data/restraints/parameters 7934/0/431, GOF = 1.03, $R_1(wR_2) = 0.041$ (0.106) ($I > 2\sigma(I)$).

3. Results and discussion

3.1. Solvatochromism of the mixed chelates

As in the case of the $[\text{Cu}(\text{acac})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ -type chelates [5,7], the trop and hino chelates prepared are all soluble in a large number of organic solvents, forming violet solutions in solvents of low DN (Gutman's donor number) [8] and changing through blue to green as the solvent DN increases.

The observed ν_{max} values of the d–d bands of the chelates in various solvents are summarized in Table 1 and plotted versus the DN of the respective solvents in Fig. 1. The ν_{max} values decrease nearly linearly with the increasing DNs of solvents. This originates in variation of the Lewis acid–base interaction between the chelate ion and the respective solvent molecule; since the d_{xy} , d_{yz} and d_{zx} orbitals of the Cu(II) ion will

Table 1

The ν_{\max} ($\times 10^3 \text{ cm}^{-1}$) values of d–d transition bands of $[\text{Cu}(\text{trop}/\text{hino})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ in various solvents^a

Solvent	DN	$[\text{Cu}(\text{trop})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$	$[\text{Cu}(\text{hino})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$	$[\text{Cu}(\text{acac})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$
1,2-Dichloroethane	0	20.33 (18.23)	20.28 (18.38)	19.98
Nitromethane	2.7	19.80 (18.69)	19.69 (18.52)	
Nitrobenzene	4.4	19.42	19.23	
1,4-Dioxane	10.8	19.23	18.69 (16.53)	18.90
Acetonitrile	14.1	17.09 (16.98)	17.09 (17.04)	17.51
Propionitrile	16.1	17.04	16.98	
Acetone	17.0	17.30 (17.27)	17.24 (17.33)	17.71
Ethanol	18.5	16.67 (16.63)	16.72 (16.72)	17.09
Methanol	19.1	16.75 (16.67)	16.72 (16.72)	17.06
Tetrahydrofuran	20.0	17.76	17.24	17.33
1- <i>n</i> -Butanol	22.0	16.72	16.81	
<i>N,N</i> -dimethylformamide	26.6	16.58 (16.34)	16.53 (16.31)	16.61
<i>N,N</i> -dimethylacetamide	27.8	16.21	16.29	16.54
Dimethylsulfoxide	29.8	16.31 (15.95)	16.26 (16.03)	16.33
Pyridine	33.1	14.45 (14.94)	14.49 (14.97)	16.58
Hexamethylphosphorous triamide	38.8	14.18	13.99	15.68

^a The results of $[\text{Cu}(\text{acac})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ are also given for comparison. The ν_{\max} ($\times 10^3 \text{ cm}^{-1}$) values of the corresponding perchlorates are in parentheses. The measurements of perchlorates were carried out in single solvent.

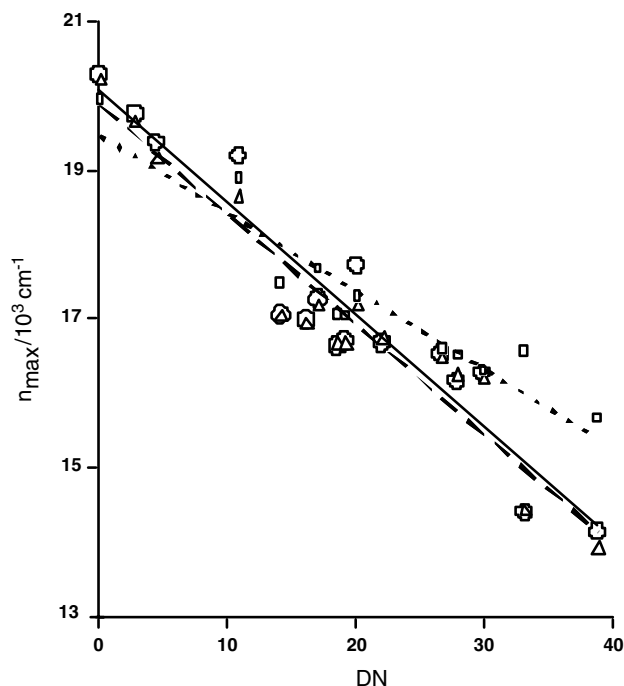


Fig. 1. Relationship between the ν_{\max} values of the d–d transition bands of $[\text{Cu}(\text{trop})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ (—, \circ) and $[\text{Cu}(\text{hino})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ (---, \triangle) in various solvents and the donor number of the respective solvents. The results of the corresponding acac analog, $[\text{Cu}(\text{acac})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$, (\cdots , \square) are given in comparison.

all be lifted up by its interaction with polar solvent molecules approaching from above and below the chelate plane, the broad d–d transition band will be shifted to lower energy region. The exceptions to this rule are found in the case of 1,2-dichloroethane for the perchlorates [9], as shown in Table 1. The ν_{\max} values in 1,2-dichloroethane (DN = 0) are notably lower than those in nitromethane (DN = 2.7). The

same anomaly was formerly found in the case of the $[\text{Cu}(\text{acac})(\text{tmen})]\text{ClO}_4$ -type chelates [10] and was shown to be due to remarkable ion-pair formation in the former solvent. If the coordinating ability of anion becomes stronger, the anion will be bound more tightly to Cu(II) ion instead of solvent molecule.

The extent of the solvatochromic spectral change may now be expressed by the difference between ν_{\max} values in two solvents of widely different DN, e.g., $\Delta = (\nu_{\max})_{\text{dce}} - (\nu_{\max})_{\text{py}}$, where dce and py mean 1,2-dichloroethane and pyridine, respectively. The Δ values of $[\text{Cu}(\text{trop})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ and $[\text{Cu}(\text{hino})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ are 5.87 and 5.79, respectively, which are larger than that of the acac chelate. In addition, the ν_{\max} values themselves for both trop and hino chelates are mostly smaller in weak donor solvents but larger in stronger donor solvents than those for the acac chelate. It is found, from the linear relationship of the ν_{\max} values with DN, the larger Δ values and the poorer donor ability of $\text{B}(\text{C}_6\text{H}_5)_4^-$ ion, that the trop and hino chelates can be used as excellent Lewis basicity indicators in solution.

3.2. Effects of various anions

Table 2(a) and (b) summarize the ν_{\max} values of $[\text{Cu}(\text{trop})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ and $[\text{Cu}(\text{hino})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ in various solvents and in the presence of various anions. In Fig. 2(a) and (b), they are also plotted for each donor solvent versus the ν_{\max} values in 1,2-dichloroethane ($\nu_{\max}(\text{dce})$), namely the ν_{\max} values of the column of left-end in the respective tables on the abscissa; for example, a coordinate of (20.00, 16.89) is given for $[\text{Cu}(\text{trop})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ in acetonitrile in the presence of BF_4^- ion. The addition of anions results in a similar effect on the spectra of both chelates. In high donor

Table 2

The ν_{\max} (10^3 cm^{-1}) values of d–d transition bands of $[\text{Cu}(\text{trop})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ (a) and $[\text{Cu}(\text{hino})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ (b) in various solvents in the presence of various anions^a

	dce	nm	an	ac	etoh	thf	dmf	dmso
(a) $[\text{Cu}(\text{trop})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$								
$\text{B}(\text{C}_6\text{H}_5)_4^-$	20.33	19.80	17.09	17.67	16.39	17.76	16.10	16.13
BF_4^-	20.00	19.84	16.89	17.67	16.42	17.70	16.10	16.13
ClO_4^-	19.76	19.84	16.69	17.67	16.37	17.70	16.10	16.13
CO_3^{2-}	18.98	19.78	16.67	17.67	16.31	17.70	16.10	16.13
CF_3SO_3^-	17.95	18.02	17.08	17.79	16.37	17.67	16.10	16.13
CH_3COO^-	16.64	16.37	16.53	17.18	16.37	16.98	16.10	15.67
Br^-	14.88	14.71	14.45	14.45	16.34	14.51	14.71	16.13
Cl^-	14.71	14.29	14.29	14.35	16.18	14.45	14.43	16.10
(b) $[\text{Cu}(\text{hino})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$								
$\text{B}(\text{C}_6\text{H}_5)_4^-$	20.62	19.69	17.67	17.89	16.53	17.79	16.23	16.26
BF_4^-	20.16	19.69	17.57	18.02	16.47	17.79	16.23	15.92
ClO_4^-	19.92	19.65	17.57	17.73	16.47	17.79	16.23	15.95
CO_3^{2-}	18.32	18.32	17.64	17.95	16.47	17.70	16.18	15.95
CF_3SO_3^-	17.79	17.86	17.36	17.64	16.47	17.64	16.23	16.05
CH_3COO^-	16.56	16.50	16.81	16.69	16.47	16.75	16.00	16.00
Br^-	14.25	14.37	14.53	14.39	16.10	14.35	14.35	14.35
Cl^-	14.14	14.22	14.10	14.14	16.00	14.14	14.14	14.14

^a Abbreviations of solvents are as follows: dce, 1,2-dichloroethane; nm, nitromethane; an, acetonitrile; ac, acetone; etoh, ethanol; thf, tetrahydrofuran; dmf, *N,N*-dimethylformamide; dmso, dimethylsulfoxide.

solvents such as dimethylsulfoxide and dimethylformamide, no variation or only a weak shift of the $\nu_{\max}(\text{solv})$ values is observed; the plot approximately follows an horizontal line. In the lowest donor solvent (1,2-dichloroethane), a continuous linearly ascending plot is obtained. The spectra in solvents of intermediate donor strength give discontinuous plots composed of a plateau at larger $\nu_{\max}(\text{dce})$ values and an ascending part at lower ones with an inclination similar to that observed for 1,2-dichloroethane solutions.

The interactions of both chelates with the anions added depend upon the donor and acceptor properties of the solvents; when the donor strength of the solvent is higher than that of the anion, the solvent molecule preferably coordinates to Cu(II) ion, while a solvent exhibiting strong acceptor properties will preferentially solvate the anion, preventing coordination of the anion to Cu(II) ion. The $\nu_{\max}(\text{solv})$ values remain constant in the region of the anions with weaker donor strength. In such “the solvent-governed” region, the constant $\nu_{\max}(\text{solv})$ values refer to the spectra of solvated $[\text{Cu}(\text{trop}/\text{hino})(\text{tmen})]^+$ and thus reflect the donor number of the solvent. Enhancing the donor properties of the anions leads to a point where the anions coordinate significantly to $[\text{Cu}(\text{trop}/\text{hino})(\text{tmen})]^+$, so that further enhancement in the donor strength of the anions leads to decreasing “anion-governed” shift of $\nu_{\max}(\text{solv})$ as same as the shifts observed for 1,2-dichloroethane solutions. The donor properties of the solvent and those of the anion become equal at the intersection point of the “solvent-governed” and “anion-governed” regions.

Fig. 3 offers a quantitative view of the competition between solvent molecule and anion for coordination

to metal. On the basis of the many ν_{\max} values published to describe solvatochromism, the solution behaviors of Lewis basicity indicators introduced in the present study and the consideration of the donor and acceptor numbers of the solvents and the donor numbers of anions [11], it is possible to predict the coordination mode of the chelate. The coordination of any anion A^- is possible within a space room defined by $\text{DN}(\text{anion}) > \text{DN}(\text{solvent})$ and $\text{AN}(\text{solvent}) < 40$. Outside the room space permitting the coordination of anion, both chelate and anion will be solvated.

3.3. Molecular structures of the trop chelates

Instead of naked unsolvated $[\text{Cu}(\text{trop})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$, single crystals of the solvated species $[\text{Cu}(\text{trop})(\text{tmen})(\text{dce})]\text{B}(\text{C}_6\text{H}_5)_4$ and $[\text{Cu}(\text{trop})(\text{tmen})(\text{ac})]\text{B}(\text{C}_6\text{H}_5)_4$ were obtained, where dce is 1,2-dichloroethane and ac is acetone. The existence of the solvated species was the evidence of weak ligand field strength of the mixed chelates, and then the studied chelates were more sensitive as the color indicator for Lewis basicities of solvent and anion. Both solvated chelates crystallize in the monoclinic space group $P2_1/n$, but differ significantly in their lattice architectures. Their crystallographic data are given in Section 2; selected bond lengths and angles are presented in Table 3, and structural views are shown in Fig. 4. Copper(II) ion exhibits in both compounds slightly twisted square planar coordinations by two tropolone oxygen atoms and two diamine nitrogen atoms with bond lengths and bond angles comparable to $[\text{Cu}(\text{trop})_2]$, $[\text{Cu}(\text{en})(1,3\text{-diketonates})](\text{en} = 1,2\text{-ethanediamine})$ and related complexes

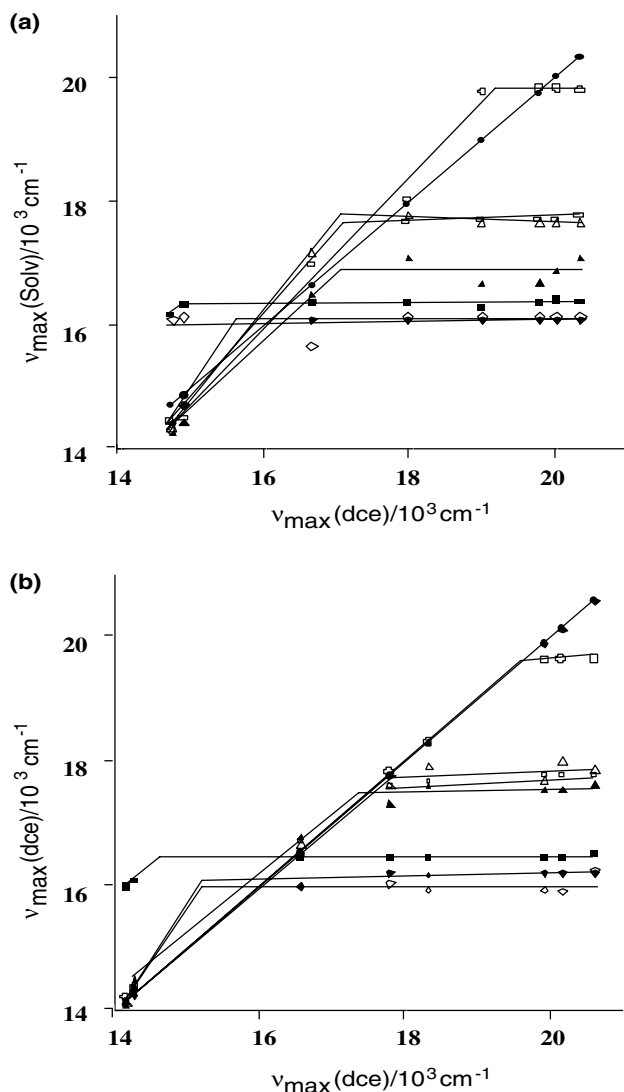


Fig. 2. (a) The ν_{\max} values of $[\text{Cu}(\text{trop})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ in 1,2-dichloroethane containing various anions dissolved in various donor solvents; dichloroethane (●), nitromethane (○), acetonitrile (▲), acetone (△), ethanol (■), tetrahydrofuran (□), dimethylformamide (◇) and dimethylsulfoxide (◆). (b) The ν_{\max} values of $[\text{Cu}(\text{hino})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ in 1,2-dichloroethane containing various anions dissolved in various donor solvents; dichloroethane (●), nitromethane (○), acetonitrile (▲), acetone (△), ethanol (■), tetrahydrofuran (□), dimethylformamide (◇) and dimethylsulfoxide (◆).

[12–16]. In $[\text{Cu}(\text{trop})(\text{tmen})(\text{dce})]\text{B}(\text{C}_6\text{H}_5)_4$, which has the stronger twisted CuO_2N_2 coordination figure (r.m.s. aplanarity 0.101 Å, Cu 0.020 Å off l.s. plane), there is one very weak axial interaction with Cl(1) of a dce molecule, $\text{Cu}–\text{Cl}(1) = 3.580$ Å, whereas the opposite side of the CuO_2N_2 moiety is shielded by a remote $\text{B}(\text{C}_6\text{H}_5)_4$ phenyl ring. This $\text{Cu}–\text{Cl}$ interaction is ~ 1 Å longer than cases with a clear-cut axial $\text{Cu}–\text{Cl}$ bond as encountered in compounds reported [17,18]. A distinctly different situation is encountered in $[\text{Cu}(\text{trop})(\text{tmen})(\text{ac})]\text{B}(\text{C}_6\text{H}_5)_4$: here two $[\text{Cu}(\text{trop})(\text{tmen})(\text{ac})]$ units are

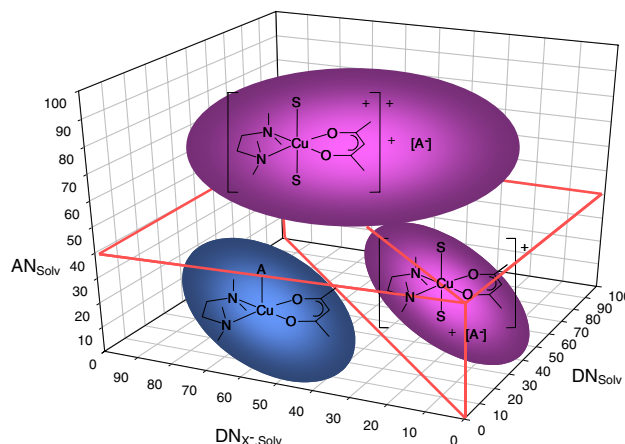


Fig. 3. A view of competition between solvent molecule and anion for coordination to metal.

π -stacked with their trop residues in C_i -related antiparallel pairs, thus mutually blocking the access to CuO_2N_2 moiety on one side, whereas on the opposite side, i.e., in

Table 3

Selected bond lengths (Å) and angles (°) for (a) $[\text{Cu}(\text{trop})(\text{tmen})(\text{dce})]\text{B}(\text{C}_6\text{H}_5)_4$ and (b) $[\text{Cu}(\text{trop})(\text{tmen})(\text{ac})]\text{B}(\text{C}_6\text{H}_5)_4$

	(a)	(b)
Cu–O(2)	1.925(1)	1.918(2)
Cu–O(1)	1.931(1)	1.930(2)
Cu–N(1)	2.007(1)	2.004(2)
Cu–N(2)	2.017(1)	2.004(2)
[Cu–Cl(1)]	3.580(1)]	
Cu–O(3)		2.502(2)
O(1)–Cu–O(2)	84.01(4)	83.16(7)
O(1)–Cu–N(1)	94.16(4)	95.12(8)
O(1)–Cu–N(2)	171.94(5)	170.70(9)
O(2)–Cu–N(1)	174.43(5)	175.21(8)
O(2)–Cu–N(2)	95.04(4)	93.74(7)
N(1)–Cu–N(2)	87.50(5)	87.27(9)
O(1)–C(1)	1.305(2)	1.279(3)
O(2)–C(7)	1.300(2)	1.288(3)
C(1)–C(2)	1.405(2)	1.399(3)
C(1)–C(7)	1.474(2)	1.457(3)
C(2)–C(3)	1.395(2)	1.370(4)
C(3)–C(4)	1.392(2)	1.368(4)
C(4)–C(5)	1.394(2)	1.369(4)
C(5)–C(6)	1.392(2)	1.391(4)
C(6)–C(7)	1.409(2)	1.392(3)
C(8)–C(9)	1.510(2)	1.343(5)
N(1)–C(8)	1.503(2)	1.435(4)
N(1)–C(10)	1.483(2)	1.455(5)
N(1)–C(11)	1.484(4)	1.448(4)
N(2)–C(9)	1.488(2)	1.481(4)
N(2)–C(12)	1.495(2)	1.463(4)
N(2)–C(13)	1.490(2)	1.480(4)
Cl(1)–C(38)	1.805(2)	
C(38)–C(39)	1.499(3)	
Cl(2)–C(39)	1.788(2)	
O(3)–C(14)		1.186(4)
C(14)–C(15)		1.463(6)
C(14)–C(16)		1.489(5)

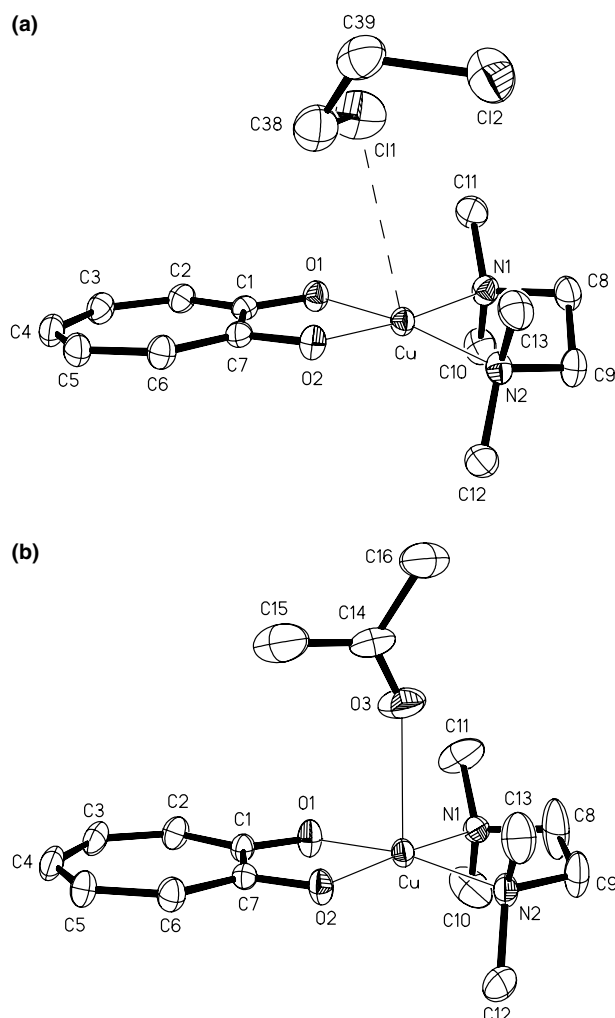


Fig. 4. Thermal ellipsoid plots of the chelate $[\text{Cu}(\text{trop})-(\text{tmen})\text{S}]\text{B}(\text{C}_6\text{H}_5)_4$ with a crystal solvent S: (a) 1,2-dichloroethane (50% ellipsoids), (b) acetone (20% ellipsoids). $\text{B}(\text{C}_6\text{H}_5)_4^-$ ion and hydrogen atoms are omitted for clarity.

exo-axial direction, the acetone molecule is firmly coordinated to Cu(II), $\text{Cu}-\text{O}(3) = 2.502 \text{ \AA}$. This corresponds to a typical Jahn-Teller 4+1 coordination with a moderately pyramidal character for CuO_2N_2 moiety (r.m.s. aplanarity 0.057 \AA , Cu 0.115 \AA off l.s. plane toward O(3), for related examples see [19,20]). Hence, both solvent molecules, dce and ac, reflect nicely their different donor properties in the solid state structures of $[\text{Cu}(\text{trop})(\text{tmen})(\text{dce})]\text{B}(\text{C}_6\text{H}_5)_4$ and $[\text{Cu}(\text{trop})(\text{tmen})(\text{ac})]\text{B}(\text{C}_6\text{H}_5)_4$. This would also establish the validity of explanation for the continuous shift of the ν_{max} values of $[\text{Cu}(\text{trop}/\text{hino})(\text{tmen})]\text{B}(\text{C}_6\text{H}_5)_4$ in various solvents.

4. Supplementary material

CCDC-187873 and 187874 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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