View Article Online / Journal Homepage / Table of Contents for this issue

PAPER

NJC
www.rsc.org/njc

Conformational dynamics of Cu(I) complexes of tripodal ligands: steric control of molecular motion†

Jing Zhang, Kam Siu, Chin H. Lin and James W. Canary*

Department of Chemistry, New York University, New York, NY 10003, USA.
E-mail: canary@nyu.edu

Received (in St Louis, MO, USA) 27th June 2005, Accepted 18th July 2005
First published as an Advance Article on the web 4th August 2005

Downloaded by University of California - Los Angeles on 01 January 2013
Published on 04 August 2005 on http://pubs.rsc.org | doi:10.1039/B509050D

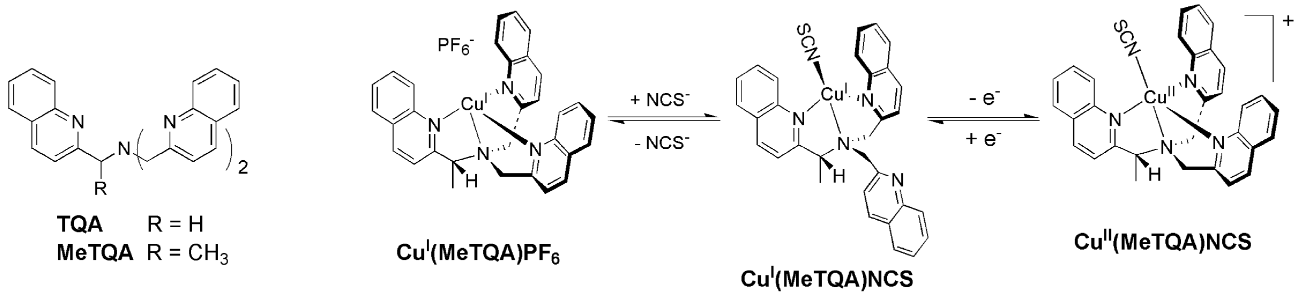
The dynamics of molecular conformational changes for Cu(I) complexes of two tripodal ligands were studied. Variable-temperature NMR and circular dichroism in combination with two-dimensional NMR experiments were employed to determine the structural and energetic details of a dynamic process in which one of three arms dissociates from coordination to Cu(I). Dissociation was triggered by addition of a strongly coordinating anion (SCN^-). One-electron oxidation to the Cu(II) complex returned coordination of all three ligand arms. The observed phenomena were dependent upon steric crowding; addition of a single methyl group to one arm resulted in marked differences in behavior. The CuSCN and $CuPF_6$ complexes of tris(2-quinolylmethyl)amine (TQA) and the $CuPF_6$ complex of 1-(quinolin-2-yl)-*N*,*N*-bis(quinolin-2-ylmethyl)ethanamine (MeTQA) did not give any evidence for differences in coordination over the temperature range 0–35 °C, while Cu^I(MeTQA)NCS demonstrated marked differences in NMR but not CD spectra over this temperature range. In the latter complex, two diastereotopic arms displace each other with a transition energy of 14.0 kcal mol^{-1}. The structure of the arm-dissociated complex contains a higher degree of stereochemical complexity than the tetradentate complexes.

Introduction

Triggered materials are of widespread interest, particularly if they may offer potential for design at the nanoscale.[1] A number of interesting studies have reported molecular systems that perform specified tasks triggered by an external input.[1–3] Among these, redox triggered optical switches have the advantage that the reading and writing events are independent phenomena, avoiding destructive readout.[4] Transition metal-based redox-triggered systems have attracted much attention recently.[5]

We have examined redox-driven conformational changes in copper coordination complexes.[4] The tripodal ligands studied contain a single stereocenter in one of the ligand arms; Cu(I/II) is coordinated such that the otherwise conformationally mobile ligand wraps around the metal, forming a propeller-like shape.[6] Inner-sphere coordination changes upon one-electron oxidation or reduction have been used to induce altered ligand conformation. Two significant changes in copper that have been exploited for these studies are the difference in hard/soft acid character between the two oxidation states of this metal, and the generally lower coordination number of Cu(I) as compared to Cu(II). For the latter case, it was found[7] that Cu(I) is ligated by all three arms of the ligand MeTQA [(*R*)-1-(quinolin-2-yl)-*N*,*N*-bis(quinolin-2-ylmethyl)ethanamine], shown in Scheme 1. However, in the presence of SCN^-, a strongly coordinating anion for copper, one of the arms is forced out of binding from the metal. In this ligand environment, Cu(I) displays four-coordination with a tetrahedral geometry, while five-coordinate Cu(II) may adopt a trigonal bipyramidal or square pyramidal geometry. Oxidation of Cu(I) to Cu(II) triggers the dissociated arm back into metal coordination. This process could be cycled repeatedly by the reduction and oxidation between Cu(I) and Cu(II).

The structural hypothesis in Scheme 1 was based primarily on detailed analysis of exciton-coupled circular dichroism (ECCD) amplitudes in our earlier study.[7] However, detailed structural questions could not be resolved such as which of the three arms dissociated, or whether all three of the arms underwent rapid interchange. There was some reason to suspect that



Scheme 1

---

† Electronic supplementary information (ESI) available: NMR spectra and calculated structures. See http://dx.doi.org/10.1039/b509050d

DOI: 10.1039/b509050d

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2005

Downloaded by University of California - Los Angeles on 01 January 2013
Published on 04 August 2005 on http://pubs.rsc.org | doi:10.1039/B509050D

the arm containing the chiral center (the "chiral" arm) in the Cu^I(MeTQA)NCS complex did not dissociate exclusively, which might be expected to induce a distortion or loss of the ECCD couplet.

The proposed structure of Cu^I(MeTQA)PF$_6$ in Scheme 1 is consistent with the available data and with reported X-ray structures of Cu complexes of the closely related ligand TQA [tris(2-quinolylmethyl)amine]. In the X-ray structure of [Cu^I(TQA)](ClO$_4$),[8] Cu(I) is located at the center of a pseudo-tetrahedral geometry, and possesses ligation to three quinolyl nitrogens and the tertiary nitrogen. The complexes Cu^I(TQA)PF$_6$ or Cu^I(MeTQA)PF$_6$, also with a weakly coordinating counter anion similar to perchlorate, should have similar structures. In one X-ray structure of a Cu(II) complex of TQA, namely [Cu^{II}(TQA)Cl]$^+$,[9] the geometry is a slightly distorted square pyramid, and Cu(II) is coordinated by three quinolyl nitrogens, a tertiary nitrogen and a chloride ion. If Cl$^-$ is replaced with SCN$^-$, as in [Cu^{II}(TQA)NCS]$^+$ or [Cu^{II}(MeTQA)NCS]$^+$, the structure should be similar. Some Cu(II) complexes exist as dimers bridged by SCN$^-$,[10] but for this type of tripodal ligand, they are typically monomers.[11] The structure of a Cu(I) complex of TQA or similar tripodal ligand with a strongly binding counter anion has not been reported. The closest structure available to represent the conformation of Cu^I(MeTQA)NCS in our structural model[7] is one in which a PPh$_3$ group displaces one arm from the other two.[8] However, PPh$_3$ is very unlike NCS$^-$ both sterically and electronically, so the actual structures of Cu^I(TQA)NCS and Cu^I(MeTQA)NCS might be different. As a molecular switch, one arm of the ligand is replaced by a strongly coordinating group (SCN$^-$) for the Cu(I) complex and pulled back into coordination for the Cu(II) complex, so the structure of Cu^I(MeTQA)NCS is fundamental and more direct data needed to be obtained.

In this study, we sought to use variable-temperature (VT) and modern 2D NMR methods to test our structural hypotheses for the Cu^I(MeTQA)$^+$ and Cu^I(TQA)$^+$ complexes. In the structure of Cu^I(MeTQA)NCS shown in Scheme 1, the proton resonances corresponding to the quinoline dissociated from Cu(I) should be inherently different from that of the associated arms, and they may or may not exchange with each other depending on the temperature. An additional goal of the study was to identify which of the quinoline arms dissociates or whether the dissociation and association of the arms are in rapid equilibrium.

Experimental

The ligands TQA [tris(2-quinolylmethyl)amine] and MeTQA [(*R*)-1-(quinolin-2-yl)-*N*,*N*-bis(quinolin-2-ylmethyl)ethanamine], and the corresponding Cu(I) complexes, were prepared as described previously.[7] The VT NMR and 2D NMR spectra were recorded on a Bruker AVANCE 400 MHz NMR spectrometer in CD$_2$Cl$_2$ (purchased from Cambridge Isotope Laboratories, Inc.). The NMR tubes were capped with septa under nitrogen and sealed with Parafilm to avoid air oxidation. Circular dichroism spectra were recorded on an AVIV model 202SF spectropolarimeter in methanol. Geometry optimization calculations were performed with Spartan software[12] using the semi-empirical PM3(tm) method.

Results and discussion

The VT NMR spectra of Cu^I(MeTQA)NCS and Cu^I(MeTQA)PF$_6$ were obtained in CD$_2$Cl$_2$ over the temperature range from 0 °C to 35 °C and are shown in Fig. 1 and 2, respectively. It is apparent that the behavior of the complex with the strongly coordinating SCN$^-$ counter ion is very different from that with the weakly coordinating PF$_6{}^-$.

VT NMR spectra of Cu^I(MeTQA)NCS from 0 °C to 35 °C showed coalescence of several peaks (Fig. 1). At 35 °C, two sets of peaks were observed with a ratio of 2 to 1. When the temperature was reduced to 20 °C, the set of peaks with the larger integrals gave significant line broadening and separation of peaks into two different resonances began to appear. At 10 °C and below, a spectrum was obtained remarkably different from that of higher temperature. In particular, the peaks at 8.7 and 7.3 ppm resolved into peaks at 8.8/8.6 ppm and 7.4/7.1 ppm, respectively. Also evident was significant change in the resonances for the methylene protons at 4.4 ppm: At lower temperature, two groups of overlapping peaks were observed. The coalescence of proton resonances upon temperature change can be explained by the dissociation of one arm forced by the strong coordinating anion, SCN$^-$. Therefore, the chemical shifts of protons on the dissociated arm become distinct from that of the associated arm. The spectrum at 35 °C indicated a structure in which two of the quinoline groups were in rapid dissociation and association equilibrium, but the spectrum at 10 °C suggested that all three quinolines experience unique magnetic environments. Theoretically, the three quinolines are always chemically and magnetically different due to the chiral environment, and the two achiral arms are diastereotopic. However, these two achiral arms are so similar as to show essentially identical resonances in ^{1}H NMR spectra.

The salt with PF$_6{}^-$ counter ion does not show coalescence of peaks (Fig. 2). Even though there is some line broadening at 30 and 35 °C, overall, there is relatively little change in the spectra from 0 °C to 35 °C. This is consistent with the earlier hypothesis that was given on the basis of circular dichroism data, suggesting that in the absence of the strongly coordinating SCN$^-$ counter ion, all three quinoline arms remain associated with Cu(I) ion. Only in the presence of a strongly coordinating counter ion does one arm of the complex dissociate from coordination.

Finally, the VT NMR spectra of Cu(I) complexes of TQA were taken revealing little if any change. Fig. 3 shows VT NMR spectra of Cu^I(TQA)NCS obtained in CD$_2$Cl$_2$ over the temperature range of −20 °C to 35 °C. Very little variation in the spectra was observed over this temperature range. At −20 °C, some of the lines began to broaden, but further temperature reduction gave no further broadening or splitting of the resonances. Similarly, little change was observed over the same temperature range for the complex Cu^I(TQA)PF$_6$

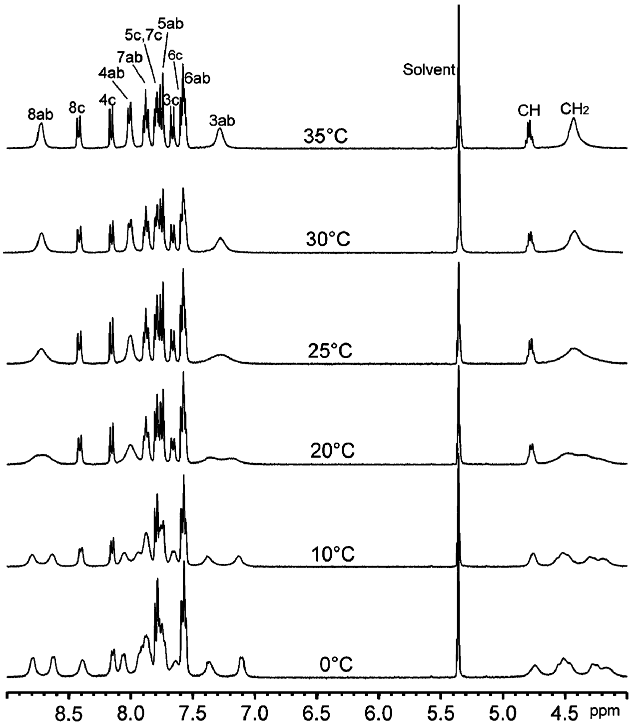


Fig. 1 VT NMR spectra of Cu^I(MeTQA)NCS in CD$_2$Cl$_2$. The designations a, b and c are discussed in the text.

Downloaded by University of California - Los Angeles on 01 January 2013
Published on 04 August 2005 on http://pubs.rsc.org | doi:10.1039/B509050D

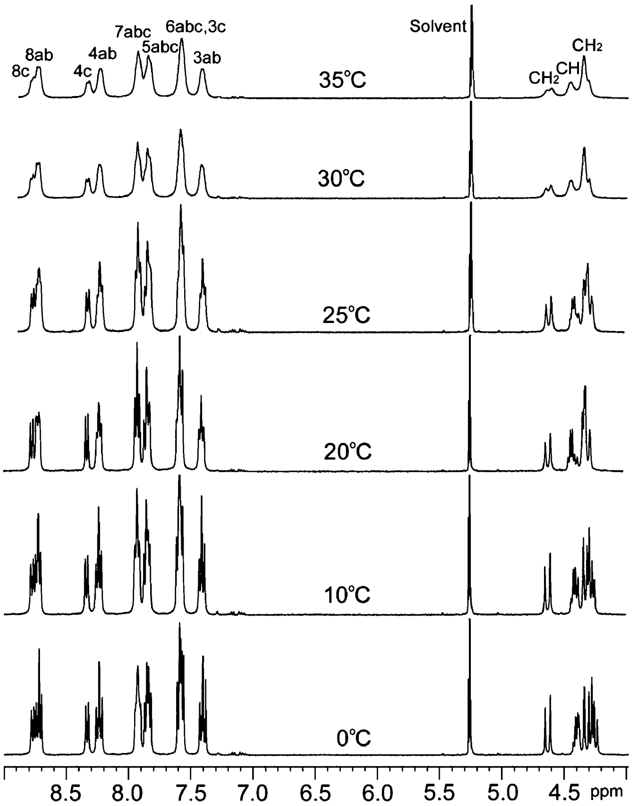


Fig. 2 VT NMR spectra of Cu^{I}(MeTQA)PF$_6$ in CD$_2$Cl$_2$. The designations a, b and c are discussed in the text.

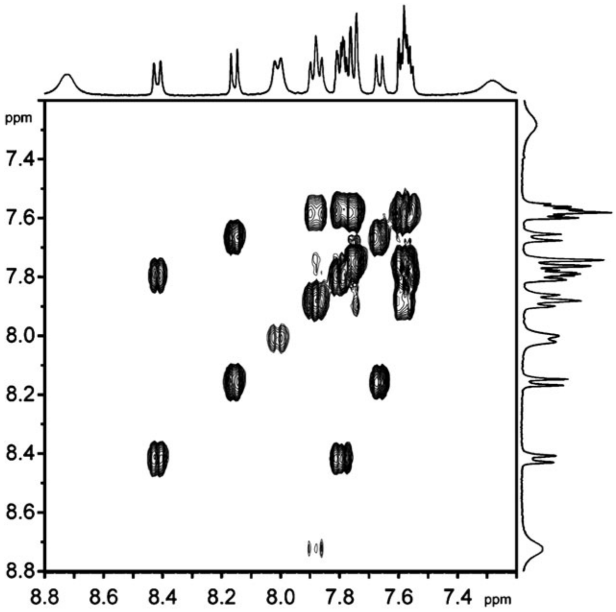


Fig. 4 COSY spectrum of Cu^{I}(MeTQA)NCS in CD$_2$Cl$_2$ at 30 °C.

(Fig. S1 in ESI†). The free ligand MeTQA also did not show a temperature-dependent H-NMR spectrum (Fig. S2 in ESI).

In order to more carefully assign the spectra of Cu^{I}(MeTQA)NCS, a series of two-dimensional spectra were obtained. Fig. 4 shows a COSY spectrum of Cu^{I}(MeTQA)NCS at 30 °C. Analysis of this spectrum shows two sets of peaks corresponding to two quinoline proton systems. With some help from integral ratio and coupling patterns of the individual resonances, each proton in the two sets of peaks was identified from the cross peaks in the COSY spectrum. The assignments are shown in Fig. 1 for spectra at 35 °C. The set of protons corresponding to two quinolines was labeled 'ab', while the set of signals that integrated to one quinoline was labeled 'c'. Some overlap in the region of 7.8 to 7.9 ppm obscured the assignment of H5 and H7. This 'ab' and 'c' labeling scheme was also applied to the proton assignments for MeTQA (Fig. S2 in ESI) and Cu^{I}(MeTQA)PF$_6$ (Fig. 2). The numbering scheme is adopted from that of quinoline, starting the numbering from the N as 1.

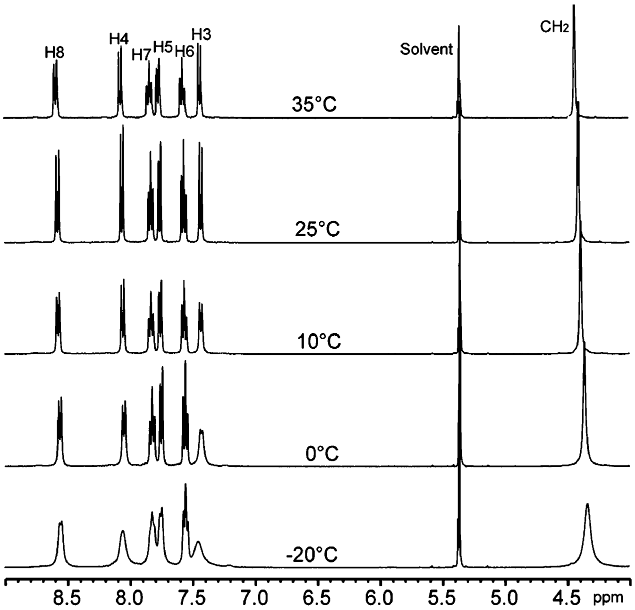


Fig. 3 VT NMR spectra of Cu^{I}(TQA)NCS in CD$_2$Cl$_2$.

With the hypothesis that the set of peaks corresponding to two quinolines derives from the arms containing methylene groups (the "achiral" arms), data were obtained regarding this point from the HMBC spectrum of this complex, which is shown in Fig. 5. HMBC indicates three-bond proton–carbon interactions. A cross peak corresponding to the proton resonance at 4.7 ppm with the carbon resonance at 58 ppm represented the interaction between the methine proton of the chiral arm and the methylene carbon of the achiral arms. Another cross peak was observed between one of the protons attached to the aromatic ring at approximately 7.6 ppm and the carbon that appears at 67 ppm, assigned to the methine carbon of the chiral arm and H3 of the quinoline attached to the chiral arm. This is also consistent with the one-proton integral of that arm and diminished intensity of the carbon compared to the other two carbons corresponding to

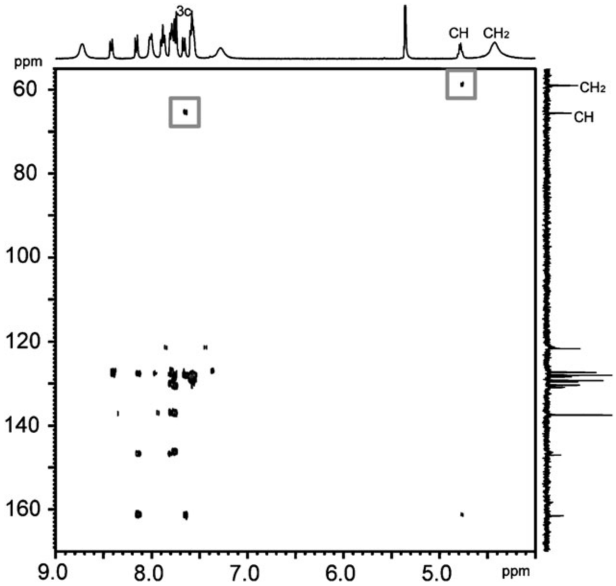


Fig. 5 HMBC spectrum of Cu^{I}(MeTQA)NCS in CD$_2$Cl$_2$ at 30 °C.

View Article Online

Downloaded by University of California - Los Angeles on 01 January 2013
Published on 04 August 2005 on http://pubs.rsc.org | doi:10.1039/B509050D

methylene in the achiral arms. Other 2D spectra included in the ESI confirm the assignments of various protons and carbons, including the assignment of which aliphatic carbon is secondary (methylene carbon) (DEPT spectrum, Fig. S6), which aliphatic carbon links to the methine proton (HSQC spectrum, Fig. S7), and which protons belong to the same aromatic ring (TOCSY spectrum, Fig. S8).

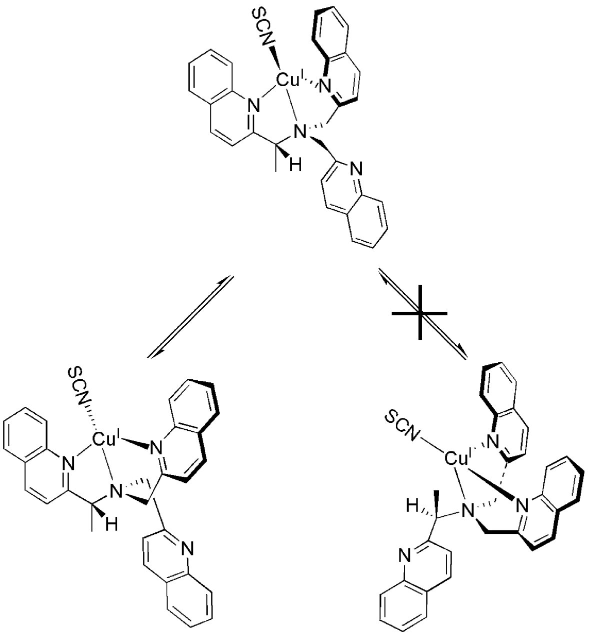
Comparing spectra of free ligand MeTQA (Fig. S2) *vs.* its Cu(I) complex (Fig. 1), we note that in the achiral arm, H8 moves downfield while H3 moves upfield. The shifts for the dissociated arm do not line up precisely with free ligand resonances due to the influence of these shifts upon both metal ion coordination and three-dimensional positioning in shielding *vs.* deshielding cones arising from the aromatic rings. Nevertheless, upon differentiation of achiral arms 'a' and 'b' at 10 °C, one of the arms demonstrates greater relative downfield shift for H8 and greater relative upfield shift for H3, consistent with one of the two arms, 'a' or 'b', being dissociated from the metal ion.

At this stage, it seemed likely that the conformationally dynamic process observed in the Cu^I(MeTQA)NCS complex only involves the dissociation and association of the two achiral quinolines. Little change in the spectrum for the resonances corresponding to the protons associated with the chiral arm was observed as a function of temperature. This suggested that the chiral arm remains associated with the metal at all times, and dissociation is restricted to the achiral arms. At 35 °C, the two achiral arms dissociate and associate rapidly on the NMR time scale providing a single set of peaks with double intensity compared to the chiral arm. At 10 °C, all three arms are differentiable, consistent with the structure of this complex shown in Scheme 2, in which one achiral arm dissociates from the metal ion, and the displacement is slow for the two achiral arms. The transition energy was calculated as 14.0 kcal mol^{-1} using eqn (1):[13]

$$\begin{aligned}\Delta G^{\neq}_{C} &= 2.3RT_{C}[10.32 + \log(T_{C}/k_{C})]\\ &= 2.3RT_{C}\left[10.32 + \log\left(\sqrt{2}T_{C}/\pi\Delta\nu\right)\right] \qquad (1)\end{aligned}$$

in which $T_C = 298$ K and $\Delta\nu = 0.38$ ppm. The conversion rate therefore is 540 s^{-1} at room temperature, when calculated by eqn (2):

$$k = C \times e^{-\Delta G^{\neq}/RT} \qquad (2)$$



Scheme 2

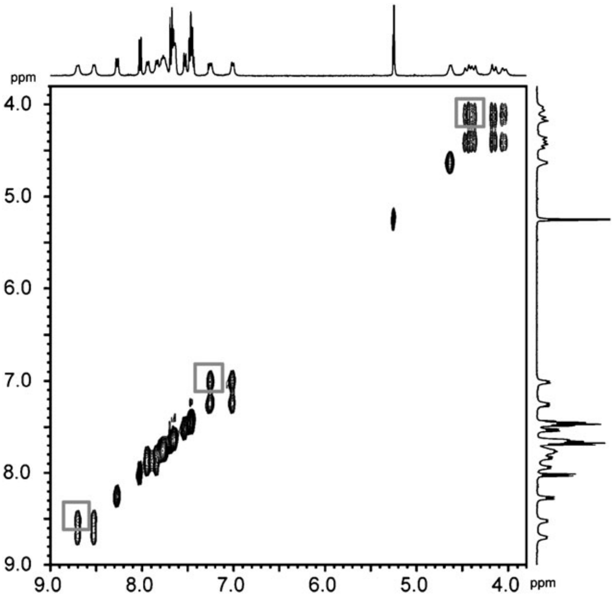


Fig. 6 2D ROESY expanded contour plot of the Cu^I(MeTQA)NCS in CD_2Cl_2 with mixing time of 200 ms at 10 °C.

To further demonstrate that the two achiral arms of Cu^I(MeTQA)NCS are in dynamic exchange, a 2D ROESY experiment with a mixing time of 200 ms was performed at 10 °C. The expanded contour plot is shown in Fig. 6. ROESY is rotating frame NOESY and commonly used for monitoring exchange processes.[14] Under these conditions, protons exchanging on the NMR time scale can be observed as off-diagonal signals. These exchange cross peaks can easily be identified because they have different phases compared to the regular cross peaks that arise from NOE. The cross peak appearing at 4.2 to 4.5 ppm corresponds to the interconversion of methylene protons on the achiral arms. Also apparent is an exchange between the peaks at 7.1 and 7.4 ppm, and also at 8.6 and 8.8 ppm. The same peaks exhibited splitting in the VT NMR spectra. The ROESY spectra, therefore, confirmed that these protons are in dynamic exchange. The 1D trace of the ROESY spectrum in Fig. 6 shows more clearly the two sets peaks between 4 and 4.5 ppm. In this region, four doublets were observed; consistent with each proton of the methylene of the achiral arms occupying a unique magnetic environment. Exchanging cross peaks were not observed for other proton resonances which are either too close in chemical shift (other protons on the achiral arms), or not exchangeable (protons on the chiral arm).

Why do only the achiral arms exhibit dissociation while the chiral arm does not? Dissociation of the latter enforces steric crowding of the methyl substituent: The steric interaction between the methyl and an adjacent quinolyl group is similar to a highly unfavorable *syn*-pentane interaction.

To check for the possibility that a change in solution equilibrium was observed over the temperature range in question, variable-temperature circular dichroism (VT CD) spectra of Cu^I(MeTQA)NCS were taken from −20 °C to 35 °C in methanol. Methylene chloride, which gave the best NMR spectra, could not be used in this CD measurement because of the 232 nm cut-off wavelength for the solvent. These CD spectra are shown in Fig. 7. Very little if any change occurs over the specified temperature range. The absence of significant change in the CD spectra is consistent with the lack of population change over the temperature range studied. The CD data also exclude other potential processes such as intermolecular interactions, which could also potentially be affected by temperature.

It was surprising to observe such different behavior for Cu^I(MeTQA)NCS compared to Cu^I(TQA)NCS. The methyl

View Article Online

Downloaded by University of California - Los Angeles on 01 January 2013
Published on 04 August 2005 on http://pubs.rsc.org | doi:10.1039/B509050D

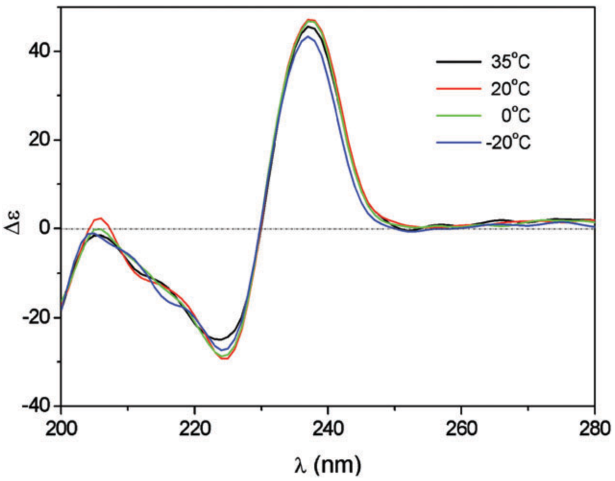


Fig. 7 Variable-temperature circular dichroism (VT CD) spectra of $Cu^I(MeTQA)NCS$ in MeOH.

group on the arm causes an increase in the interconversion barrier, making the arm displacement of $Cu^I(MeTQA)NCS$ observable at room temperature. Among the three arms of the MeTQA ligand, the methyl group creates a steric situation in which the chiral arm does not exchange on the same timescale as the achiral arms. A substituent on one of the arms plays a critical role on controlling which arm will translocate.

Finally, it is of interest to draw attention to a stereochemical consequence of the dynamic behavior of these complexes: Arm-dissociation for $Cu^I(MeTQA)NCS$ results in lower overall symmetry of the complex. In the Cu(II) and $Cu^I(MeTQA)PF_6$ complexes, the two achiral arms, which remain coordinated to the metal, are diastereotopic. As such, those complexes possess two chiral elements, the chiral carbon center and the helicity of the propeller shape formed by the planes of the three heterocycles. In the arm-dissociated structure for $Cu^I(MeTQA)NCS$ shown in Scheme 1, all three ligand arms are distinct. In such a circumstance, the tertiary nitrogen atom of the ligand and the copper ion become centers of chirality, in addition to the carbon center and the helix axis resulting from the twist of the overall complex. Thus, this structure contains a total of four elements of chirality, with three points and one axis. Three of these four chiral elements are formed upon complexation of the ligand with a metal ion. Of course, these highly unsymmetrical complexes interconvert at room temperature on the NMR time scale, with arm exchange inverting the stereochemistry at the nitrogen and copper centers.

Conclusion

The data are fully consistent with the structural hypothesis forwarded in previous publications[7] based on circular dichroism spectra. The structures of $Cu^I(TQA)PF_6$ and $Cu^I(MeTQA)PF_6$ are fully symmetrical and consistent with tetradentate ligand coordination as shown in Scheme 1.

$Cu^I(MeTQA)NCS$ shows strong changes in the NMR spectra over the range 0–35 °C. The protons in the Cu(I) complexes were assigned by a combination of 2D NMR methods. The low-temperature structure has therefore been assigned with one arm dissociated as shown in Scheme 1. The VT NMR spectra of $Cu^I(MeTQA)NCS$ are consistent with interchange of the two methylene-containing arms of the ligand. No evidence for dissociation of the arm containing the chiral carbon center was observed. The invariance of the CD spectra over the same temperature range shows that at higher temperature the same relative populations of conformers persist as at lower temperature.

Therefore, not only have we been able to obtain confirmatory data for our earlier structural hypothesis, but we have also been able to assign which of the three arms of the tripodal ligand is able to dissociate. The presence of the additional methyl substituent in MeTQA imparts significantly altered conformational dynamics, and allows control as to which of the three arms may dissociate from the metal. This stereodynamic control of molecular conformational behavior is particularly interesting in the context of redox-triggered nanoscale materials.

Acknowledgements

This work was supported by National Science Foundation Grants 0316589, 0234863, and 0116222.

References

1 (*a*) V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines – A Journey into the Nanoworld*, Wiley-VCH, Weinheim, Germany, 2003; (*b*) *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, Germany, 2001.

2 (*a*) J. Zhang, M. T. Albelda, Y. Liu and J. W. Canary, *Chirality*, 2005, **17**, 404–420; (*b*) F. M. Raymo and M. Tomasulo, *Chem. Soc. Rev.*, 2005, **34**, 327–336; (*c*) C. J. Easton, S. F. Lincoln, L. Barr and H. Onagi, *Chem. Eur. J.*, 2004, **10**, 3120–3128; (*d*) A. H. Flood, J. F. Stoddart, D. W. Steuerman and J. R. Heath, *Science*, 2004, **306**, 2055–2056.

3 (*a*) R. A. van Delden, M. K. J. ter Wiel and B. L. Feringa, *Chem. Commun.*, 2004, **2**, 200–201; (*b*) Y. Liu, A. H. Flood and J. F. Stoddart, *J. Am. Chem. Soc.*, 2004, **126**, 9150–9151; (*c*) J. Heinze, C. Willmann and P. Bäuerle, *Angew. Chem., Int. Ed.*, 2001, **40**, 2861–2864; (*d*) A. Petitjean, R. G. Khoury, N. Kyritsakas and J.-M. Lehn, *J. Am. Chem. Soc.*, 2004, **126**, 6637–6647; (*e*) Y.-D. Cao, Q.-Y. Zheng, C.-F. Chen and Z.-T. Huang, *Tetrahedron Lett.*, 2003, **44**, 4751–4755; (*f*) G. Ambrosi, P. Dapporto, M. Formica, V. Fusi, L. Giorgi, A. Guerri, M. Micheloni, P. Paoli, R. Pontellini and P. Rossi, *Chem. Eur. J.*, 2003, **9**, 800–810; (*g*) R. Rathore, P. L. Magueres, S. V. Lindeman and J. K. Kochi, *Angew. Chem., Int. Ed.*, 2000, **39**, 809–812; (*h*) D. -H. Qu, Q.-C. Wang, J. Ren and H. Tian, *Org. Lett.*, 2004, **6**, 2085–2088; (*i*) R. A. van Delden, N. P. M. Huck, J. J. Piet, J. M. Warman, S. C. J. Meskers, H. P. J. M. Dekkers and B. L. Feringa, *J. Am. Chem. Soc.*, 2003, **125**, 15659–15665; (*j*) J. -I. Nishida, T. Suzuki, M. Ohkita and T. Tsuji, *Angew. Chem., Int. Ed.*, 2001, **40**, 3251–3254; (*k*) D. W. Steuerman, H.-R. Tseng, A. J. Peters, A. H. Flood, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart and J. R. Heath, *Angew. Chem., Int. Ed.*, 2004, **43**, 6486–6491.

4 J. W. Canary and S. Zahn, *Trends Biotechnol.*, 2001, **19**, 251–255.

5 (*a*) S. Zahn and J. W. Canary, *Science*, 2000, **288**, 1404–1407; (*b*) D. Kalny, M. Elhabiri, T. Moav, A. Vaskevich, I. Rubinstein, A. Shanzer and A-M. Albrecht-Gary, *Chem. Commun.*, 2002, 1426–1427; (*c*) X. Guo, D. Zhang, H. Tao and D. Zhu, *Org. Lett.*, 2004, **6**, 2491–2494; (*d*) C. Sporer, I. Ratera, D. Ruiz-Molina, Y. Zhao, J. Vidal-Gancedo, K. Wurst, P. Jaitner, K. Clays, A. Persoons, C. Rovira and J. Veciana, *Angew. Chem., Int. Ed.*, 2004, **43**, 5266–5268; (*e*) S. Sortino, S. Petralia and S. Di Della, *J. Am. Chem. Soc.*, 2003, **125**, 5610–5611; (*f*) L. Fabbrizzi, M. Licchelli, S. Mascheroni, A. Poggi, D. Sacchi and M. Zema, *Inorg. Chem.*, 2002, **41**, 6129–6136; (*g*) A. Dei, D. Gatteschi, C. Sangregorio and L. Sorace, *Acc. Chem. Res.*, 2004, **37**, 827–835.

6 (*a*) J. W. Canary, C. S. Allen, J. M. Castagnetto and Y. Wang, *J. Am. Chem. Soc.*, 1995, **117**, 8484–8485; (*b*) Y.-H. Chiu, O. dos Santos and J. W. Canary, *Tetrahedron*, 1999, **55**, 12069–12078.

7 (*a*) S. Zahn and J. W. Canary, *J. Am. Chem. Soc.*, 2002, **124**, 9204–9211; (*b*) S. Zahn and J. W. Canary, *Angew. Chem., Int. Ed.*, 1998, **37**, 305–307.

8 N. Wei, N. N. Murthy, Q. Chen, J. Zubieta and K. D. Karlin, *Inorg. Chem.*, 1994, **33**, 1953–1965.

9 N. Wei, N. N. Murthy and K. D. Karlin, *Inorg. Chem.*, 1994, **33**, 6093–6100.

10 M. Biagini Cingi, A. M. Manotti Lanfredi and A. Tiripicchio, *Inorg. Chim. Acta*, 1983, **72**, 81–88.

11 M. Di Vaira and F. Mani, *J. Chem. Soc., Dalton Trans.*, 1985, 2327–2332.

12 SPARTAN SGI version 5.1.3, Wavefunction, Inc., Irvine, CA 92612.

13 J. B. Lambert, H. F. Shurvell, D. A. Lightner and R. G. Cooks, *Organic Structural Spectroscopy*, Prentice-Hall, Upper Saddle River, New Jersey, 1998.

14 H.-J. Schneider, F. Hacket, V. Rüdiger and H. Ikeda, *Chem. Rev.*, 1998, **98**, 1755–1785.