A series of luminescent Cu(1) mixed-ligand complexes containing 2,9-dimethyl-1,10-phenanthroline and simple diphosphine ligands†‡

Ken Saito, Takashi Arai, Naoki Takahashi, Toshiaki Tsukuda and Taro Tsubomura*

Received 19th June 2006, Accepted 10th August 2006 First published as an Advance Article on the web 18th August 2006 DOI: 10.1039/b608641a

A series of Cu(1) mixed-ligand complexes containing dmp (2,9-dimethyl-1,10-phenanthroline) and one of simple diphosphine ligands (Ph₂P(CH₂)_nPPh₂) were prepared. Among the complexes, [Cu(dppp)(dmp)]PF₆ (n = 3) and [Cu₂(dppb)₂(dmp)₂](PF₆)₂ (n = 4) were characterized by X-ray structure analyses. The dppp complex has been characterized as a mononuclear complex, while [Cu₂(dppb)₂(dmp)₂]²⁺ exists as a dinuclear complex in which two dppb ligands bridge between the two Cu(1) atoms. Although the distorted tetrahedral structures around the central metals of the two complexes are similar, the P–Cu–P angles are different between the two complexes. All of the series of complexes show photoluminescence in solution, and the intensity of the luminescence increases with n (n = 2–4). The non-radiative rate constants of the complexes are similar.

Introduction

There has been an increasing interest in the photophysics and photochemistry of Cu(I) complexes in the last few decades.¹ Although extensive studies on the luminescence of [Cu(diimine)₂]⁺ type complexes have been made,² the quantum yields (Φ) of the luminescence are generally low; for example, it is 0.04% for $[Cu(dmp)_2]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline).³ Special structural features are required to achieve highly luminescent species for bis(diimine)Cu(I) complexes.⁴ The mixedligand complexes of phosphines and diimines have also been studied as interesting emitters in solution.⁵ In recent years, Cu(I) complexes containing diphosphines which have a hetero atom, e.g. DPEphos (= bis[2-(diphenylphosphino)phenyl]ether)⁶ and bis(2-(diisobutylphosphino)phenyl)amide⁷ have received much attention as very strong emitters in solution. We also have been studying the synthesis of mixed-ligand Cu(I) complexes, and found that [Cu(binap)(dmp)]PF68 shows emission in CH₂Cl₂ solution (binap = 2,2'-bis(diphenylphosphino)-1,1'binaphthyl), and the quantum yield of the luminescence is similar to that of $[Cu(dppe)(dmp)]^+$ ($\Phi = 1\%)^6$ (dppe = 1,2bis(diphenylphosphino)ethane). Recently, we studied the photophysical properties of the mixed-ligand complexes containing dmp and a series of simple diphosphines, $Ph_2P(CH_2)_nPPh_2$ (n = 2-5). In this article, we show that the Cu(I) mixed-ligand complexes of the simple ligands can become good emitters.

Result and discussion

Synthesis

The mixed-ligand complexes were prepared in a similar manner to that described in refs. 6 and 8. Reactions of $[Cu(MeCN)_4]PF_6^9$ with dmp and diphosphine ligands with a molar ratio of 1 : 1 : 1 in CH₂Cl₂ gave the complexes of the empirical formula, $[Cu(Ph_2P(CH_2)_nPPh_2)(dmp)]PF_6$ (n = 2, 3, 4 and 5). The complexes are obtained as orange powders and are soluble in polar organic solvents such as dichloromethane and acetonitrile. The dppp and dppb complexes were obtained as crystals of X-ray quality by recrystallization (dppp = 1,3-bis(diphenylphosphino)propane), dppb = 1,4-bis(diphenylphosphino)butane).

Crystal structures

The crystal structure of $[Cu(dppe)(dmp)]PF_6$ was published by Coppens *et al.*,¹⁰ and its distorted tetrahedral structure was clarified. In the present study, the crystal structure of the mixed-ligand complexes containing dmp and dppp or dppb have been successfully analyzed. The crystal structure of $[Cu(dppp)(dmp)]PF_6$ has a mononuclear structure similar to the dppe complex. On the other hand, the crystal of the mixed-ligand complex containing dmp and dppb reveals a dinuclear structure.

Fig. 1 and 2 show the structure of the mononuclear cation, $[Cu(dppp)(dmp)]^+$, and the dinuclear cation, $[Cu_2(dppb)_2(dmp)_2]^{2+}$, respectively. An asymmetric unit of the crystal of the dppp complex consists of two $[Cu(dppp)(dmp)]^+$ cations and two PF_6^- anions, and that of the dppb complex consists of a half part of the $[Cu_2(dppb)_2(dmp)_2]^{2+}$ cation, one PF_6 anion and two benzene molecules. For the dppb complex, four F atoms in one of the PF_6 anions were disordered over two sites on an equatorial plane. Although the nuclearity of $[Cu_2(dppb)_2(dmp)_2](PF_6)_2$ is completely different from that of $[Cu(dppe)(dmp)]PF_6$ and $[Cu(dppp)(dmp)]PF_6$, the geometry around each copper atom

Department of Materials and Life Science, Seikei University, Kichijoji-Kitamachi, Musashino, Tokyo, 1808633, Japan. E-mail: tsubomura@ st.seikei.ac.jp; Fax: +81-422-37-3871; Tel: +81-422-37-3752

 [†] The HTML version of this article has been enhanced with colour images.
 ‡ Electronic supplementary information (ESI) available: Fig. S1: Absorption and corrected emission spectrum of [Cu(dmp)(Ph₂P(CH₂)₅PPh₂)]PF₆.
 See DOI: 10.1039/b608641a



Fig. 1 Molecular structure of $[Cu(dpp)(dmp)]^+$ with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted. The data were obtained at -150 °C. One of the two complex cations is shown. Selected bond lengths (Å) and angles (°): Cu1–P1 2.2605(9), Cu1–P2 2.2273(9), Cu1–N1 2.097(3), Cu1–N2 2.071(3); P1–Cu1–P2 105.42(3), N1–Cu1–N2 81.3(1). The parameters of the other complex cation are as follows: Cu2–P3 2.2362(9), Cu2–P4 2.2620(9), Cu2–N3 2.075(3), Cu2–N4 2.073(3); P3–Cu2–P4 105.31(3), N3–Cu2–N4 81.8(1).



Fig. 2 Molecular structure of $[Cu_2(dppb)_2(dmp)_2]^{2+}$ with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted. The data were obtained at 22 °C. An inversion centre is located at the centre of the complex. The atoms marked with * are at equivalent positions (1 - x, -y, -z). Selected bond lengths (Å) and angles (°): Cu1–P1 2.3002(14), Cu1–P2 2.256(1), Cu1–N1 2.105(4), Cu1–N2 2.117(4); P1–Cu1–P2 126.38(5), N1–Cu1–N2 80.1(2).

in the dinuclear complex is similar to that of the mononuclear dppp and dppe complexes. In those complexes, both Cu(I) atoms are surrounded by P_2N_2 donor atoms and they form distorted tetrahedra.

The Cu–P and Cu–N bond lengths are in the range 2.22–2.26 and 2.07–2.10 Å, respectively, in both the complexes. There are no significant differences in the bond lengths between the dppp and dppb complexes. However, the bond angles around the copper atoms depend largely on the diphosphines. The P–Cu–P angles of the three complexes increase with the number of methylene carbon atoms between the two phosphorous atoms (n = 2-4). Literature values for the P–Cu–P angle in the dppe and

dppp chelates fall within $90 \pm 1^{\circ 11}$ and $100 \pm 6^{\circ}$,¹² respectively. Our result of [Cu(dppp)(dmp)]PF₆ shows angles of 105–106°. On the other hand, the P–Cu–P angle in [Cu₂(dppb)₂(dmp)₂]²⁺ is 126.38(5)°. This implies that the PPh₂ groups in the dppb complex are sterically closer to the dmp ligand than in the dppe or dppp complexes.

There are some close interligand $C \cdots C$ or $C \cdots N$ distances between the dmp ligand and the phenyl groups of the diphosphine ligands. The shortest nonbonding interaction in each of the complex cations is shown in Fig 3. The nonbonding $C \cdots C$ or $C \cdots N$ distances are similar in the three complex cations, which are in the range 3.34–3.35 Å. However, the orientation of the phenyl groups is markedly different between the dppp and dppb complexes. As shown in Fig. 3, one of the phenyl groups attached to the P1 atom in the dppb ligand is located just over the Cu atom. The dihedral angle between the phenyl group and the dmp ligand is 22°. One more phenyl group attached to the P2* atom is located near the copper atom, where the closest $C \cdots N$ distance is 3.509(8) Å, although the phenyl ring is near perpendicular orientation with respect to the dmp ligand; the dihedral angle is 75°. Thus, the copper atom is effectively protected by the phenyl rings on both



Fig. 3 Drawings of the copper complexes viewed along the two phosphorous atoms of the diphosphine ligands. (a), (b) The two complex cations found in the crystal of the [Cu(dppp)(dmp]]⁺ complex cation. (c) The complex cation [Cu₂(dpp)₂(dmp)₂]²⁺. The closest interligand $C \cdots C$ or $C \cdots N$ distances in each cation is shown with both-side arrows. The distances are (a) 3.340(5), (b) 3.350(4), (c) 3.346(8) Å.

sides of the copper centre in the dppb complex. On the other hand, in the dppp complex, all the phenyl groups of the diphosphine ligands are oriented away from the copper centre as shown in Fig. 3.

Spectroscopic properties

All the mixed-ligand complexes containing $Ph_2P(CH_2)_nPPh_2$ (n = 2-5) show photoluminescence both in the solid state and in degassed CH_2Cl_2 solution. The orange-colored complex of n = 5 is strongly luminescent in solution, but the product has not yet been fully characterized. Thus, the discussion about the photophysical properties of the n = 5 complex is omitted in this paper. Absorption and luminescence spectra of the complex are shown in ESI.[‡]

Fig. 4 shows the absorption spectra of the three complexes (n = 2, 3 and 4) measured in CH₂Cl₂ solution. For the three complexes, absorption bands of moderate intensities ($\varepsilon = 2000$ - $3000 \text{ M}^{-1} \text{ cm}^{-1}$) are observed in the region 350-450 nm, which are characterized as MLCT involving the π^* orbitals of the dmp ligand of the mixed-ligand complex. The λ_{abs} of these complexes containing dppe, dppp and dppb are 405, 391 and 382 nm, respectively. A tendency is shown that the λ_{abs} shifts to higher energy as the carbon chain within the diphosphine chelate becomes longer. The correlation of the blue-shift and the geometry of the Cu(I) mixed-ligand complexes has already been discussed.¹³ Small absorption shoulders seen near 470 nm should be originated by $[Cu(dmp)_2]^+$, which is produced by a disproportionation reaction of the mixed-ligand complexes. However, each NMR spectrum of $[Cu(dppe)(dmp)]^+$, $[Cu(dppp)(dmp)]^+$ and $[Cu_2(dppb)_2(dmp)_2]^{2+}$ shows one broad signal in addition to the septet signal of PF_6^- . The broadening of the signal is characteristic of Cu(I) complexes. Given the molar absorption coefficient of [Cu(dmp)₂]⁺ is large (7800 M⁻¹cm⁻¹),³ the concentration of the minor species should be low in each solution; this accounts for the single broad NMR signal in each spectrum.



Fig. 4 Room-temperature electronic absorption spectra of (a) $[Cu(dppe)(dmp)]^+$, (b) $[Cu(dppp)(dmp)]^+$ and (c) $[Cu_2(dppb)_2(dmp)_2]^{2+}$. These spectra are measured in degassed CH_2Cl_2 The molar absorption coefficients were calculated as the complexes were all mononuclear.

Fig. 5 shows the emission spectra of these complexes in CH_2Cl_2 solution. These spectra also show the tendency of a blue shift of the λ_{em} with increase of the carbon chain within the diphosphine chelates. Moreover, the intensities of the luminescence increase with the length of the carbon chain. The dinuclear dppb complex

Table 1The photophysical properties of Cu complexes containingdiphosphine ligand(s) measured in CH_2Cl_2 solution

Diphosphine	dppe"	dppp ^b	dppb ^b
λ_{abs}/nm	405	391	382
λ_{em}/nm	594	600	590
Φ	0.01	0.037	0.10
τ/µs	1.33	5.4	10.8
$k_{\rm r}/{\rm s}^{-1}$	7.5×10^{3}	7.6×10^{3}	1.1×10^{4}
$k_{ m nr}/ m s^{-1}$	7.4×10^{5}	1.8×10^{5}	8.1×10^4

^a Cited from ref. 6. ^b The data were collected at 20 °C.



Fig. 5 Corrected emission spectra of (a) $[Cu(dppe)(dmp)]^+$, (b) $[Cu(dppp)(dmp)]^+$ and (c) $[Cu_2(dppb)_2(dmp)_2]^{2+}$ measured in degassed CH_2Cl_2 ($[Cu] = 5 \times 10^{-5}$ M) at room temperature.

has proved to be a strong emitter ($\Phi = 0.10$). Similarly, it turned out that the luminescence lifetime becomes longer with the length of the carbon chain within the diphosphine ligands. Furthermore, the values of comparatively long τ suggest the involvement of ³MLCT in the luminescence of the complexes.

Table 1 summarizes the photophysical properties of the complexes. The rate constants of radiative (k_r) and nonradiative processes (k_{nr}) calculated from Φ and τ are included. The k_r values slightly increase from the dppe complex to dppb complex. However, it turns out that the increase of the emission intensity with the length of the carbon chain in the diphosphines is mainly due to the marked decrease in the k_{nr} values. It is well known that there is a close relation between the bulkiness of the ligands around the copper centre and the intensity of the luminescence.⁴ The bulkiness of the ligand should prevent the complexes to distort in the excited states. The distortion causes the increase of the non-radiation process. Simultaneously, the bulkiness of the ligand prevents the solvent molecule to approach to the metal centre. This may be the reason why the increase of P–Cu–P angle results in a marked decrease of radiationless deactivation processes.

Conclusion

In conclusion, for the Cu(I) mixed-ligand complexes containing dmp and simple diphosphine ligands (Ph₂P(CH₂)_nPPh₂), we found that the quantum yield and lifetime of the luminescence increase with n (from n = 2 to 4). Especially for n = 4, the complex was found to have a dimeric structure and to be a strong emitter. The correlation between the P–Cu–P angles and the photophysical Downloaded by UNIVERSITY OF ALABAMA AT BIRMINGHAM on 13 January 2013 Published on 18 August 2006 on http://pubs.rsc.org | doi:10.1039/B608641A properties found in this system may be interpreted from the viewpoint of the bulkiness around the metal centre.

Experimental

General

The preparation of the mixed-ligand complexes was conducted under an Ar atmosphere using standard Schlenk tube techniques although the products are stable in air. CHN analyses of the complexes were performed on the Perkin-Elmer model 2400. NMR spectra were obtained using JEOL Λ -400 spectrometer.

Synthetic procedure and characterization

The mixed-ligand complexes, $[Cu(dmp)(Ph_2P(CH_2)_nPPh_2)]PF_6$ (n = 2, 3, 4 and 5), were prepared by reaction of $[Cu(MeCN)_4]PF_6$ with 2,9-dimethyl-1,10-phenanthroline and Ph_2P(CH_2)_nPPh_2 (n = 2-5). $[Cu(dppe)(dmp)]PF_6.^6$ $[Cu(CH_3CN)_4]PF_6^9$ (0.37 g, 1 mmol), dmp (2,9-dimethyl-1,10-phenanthroline) (0.22 g, 1 mmol) and dppe (0.40 g, 1 mmol) were dissolved in CH_2Cl_2 (15 ml). After stirring for 90 min at room temperature, the addition of diethyl ether to the solution of the complex gave a yellow powder of the mixed-ligand complex, $[Cu(dppe)(dmp)]PF_6$. The complex was obtained by filtration, and dried in *vacuo*. Yield, 85%.

Other mixed-ligand complexes were prepared from $[Cu(MeCN)_4]PF_6$, dmp and diphosphine in CH_2Cl_2 in a similar manner to that described above, dppp, dppb and 1,5-dppp (1,5-bis(diphenylphosphino)pentane) were used as diphosphine ligands.

[Cu(dppp)(dmp)]PF₆·Et₂O. Yield, 84%. Anal. Calc. for $C_{45}H_{48}CuF_6N_2OP_3$: C, 59.83; H, 5.36; N, 3.10. Found: C, 60.02; H, 5.25; N, 3.32%. ³¹P{¹H} NMR (CDCl₃) δ –8 (br).

 $\label{eq:cu2} \begin{array}{l} \mbox{[Cu2(dppb)_2(dmp)_2](PF_6)_2. Yield, 80%. Anal. Calc. for} \\ C_{84}H_{80}Cu_2F_{12}N_4P_6; C, 59.68; H, 5.01; N, 3.31. Found: C, 60.13; \\ H, 4.69; N, 3.35\%$. $^{31}P{^1H} NMR (CDCl_3) \delta -18 (br). \end{array}$

[Cu(dmp)(PPh₂(CH₂)₅PPh₂)]PF₆. Yield, 83%. Anal. Calc. for $C_{43}H_{42}CuF_6N_2P_3 : C, 60.25; H, 4.94; N, 3.27.$ Found: C, 59.77; H, 4.96; N, 3.18%. ³¹P{¹H} NMR (CDCl₃) δ –16 (br).

Data collection and reduction for X-ray crystallographic analyses

[Cu(dppp)(dmp)]PF₆. The single crystals for X-ray structural analysis were obtained by slow diffusion of *n*-heptane into a CH₂Cl₂ solution of the complex. All measurements were made on a Rigaku Saturn CCD area detector with graphite-monochromated Mo-Ka radiation. The crystal-to-detector distance was 54.90 mm. The data were collected at a temperature of -150 ± 1 °C to a maximum 2θ value of 55.0°. 1800 oscillation images were collected. Of the 67721 reflections that were collected, 16446 were unique $(R_{int} = 0.048)$; equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku).14 A numerical absorption correction was applied which resulted in transmission factors ranging from 0.86 to 0.94. The structure was solved by direct methods¹⁵ and was expanded using Fourier techniques.¹⁶ The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically and the rest were refined using the riding model. All calculations were performed using the

CrystalStructure¹⁷ crystallographic software package except for refinement, which was performed using SHELXL-97.¹⁸

[Cu(dpp)(dmp)]PF₆: C₄₁H₃₈CuN₂P₃F₆, $M_r = 829.19$, monoclinic, space group = P_{2_1}/a (no. 14), a = 17.2378(9), b = 15.4342(7), c = 28.742(1) Å, $\beta = 102.727(1)^\circ$, V = 7459.1(6) Å³, $\mu = 7.8$ cm⁻¹, Z = 8, $D_c = 1.477$ g cm⁻³, No. of unique reflections ($2\theta < 55^\circ$) = 16446, $R_1 = 0.067$ ($I > 2\sigma(I)$), $wR_2 = 0.142$ (all data), GOF = 1.22. Highest peak and deepest hole in the last difference Fourier map were 0.72 and -0.53 e Å⁻³, respectively.

[Cu₂(dppb)₂(dmp)₂](PF₆)₂. The single crystals for X-ray structural analysis were obtained by slow diffusion of benzene into an acetone solution of the complex. Data were collected on an automated Rigaku AFC5S diffractometer using graphitemonochromated Mo-K α radiation ($\lambda = 0.71069$ Å) at 23 °C. Three standard reflections were measured in every 150 reflections. An empirical absorption correction based on azimuthal scans of several reflections was applied. Calculations were carried out by using teXsan.¹⁹ The structures were solved by a direct method and refined by full-matrix least-squares methods.¹⁸ Hydrogen atoms were placed at the idealized positions, and the coordinates and the isotropic temperature factors were fixed. Anisotropic temperature factors were used for all non-hydrogen atoms except for the atoms shown below. Drawings were generated by ORTEP III.²⁰

[Cu₂(dppb)₂(dmp)₂](PF₆)₂·4C₆H₆: C₁₀₈H₁₀₆Cu₂N₄P₆F₁₂, $M_r =$ 1998.87, triclinic, space group $P\bar{1}$, a = 13.380(5), b = 17.163(3), c = 11.366(2) Å, a = 101.27(2), $\beta = 91.44(2)$, $\gamma = 79.57(2)^{\circ}$, V = 2517(1) Å³, $\mu = 5.9$ cm⁻¹, Z = 1, $D_c = 1.32$ g cm⁻³, ω -2 θ scan method, No. of unique reflections ($2\theta < 50^{\circ}$) = 8853, $R_1 = 0.063$ ($I > 2\sigma(I)$), $wR_2 = 0.164$ (all data), GOF = 1.017. Highest peak and deepest hole in the last difference Fourier map were 0.51 and -0.43 e Å⁻³, respectively.

CCDC reference numbers 602727 and 611492.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608641a

Optical spectroscopy

The absorption and luminescence spectroscopy of the mixedligand complexes in CH_2Cl_2 solution were measured using a quartz cell connected to a glass tube and a Teflon stop-cock. All samples were thoroughly deoxygenated by successive freeze–pump–thaw cycles. Absorption and luminescence spectra were measured with a Shimadzu UV-2100 spectrophotometer and a Shimadzu RF-5000 fluorometer, respectively. Luminescence decay curves were measured on a laboratory-made apparatus; the sample was excited using a nitrogen laser (USHO AN-200) and the emission light was focused into a Jobin-Yvon H-20 monochromator equipped with a Hamamatsu R955 photomultiplier. The output of the photomultiplier was digitized by a Iwatsu–Lecroy DS4262 digital oscilloscope and then downloaded to a PC.

Emission quantum yields, Φ , were measured in a deaerated (freeze-pump-thaw cycles) CH₂Cl₂ solution at 20 ± 1 °C with the use of [Ru(bpy)₃](PF₆)₂ in CH₃CN as a standard ($\Phi = 0.09$).²¹ The emission spectra were corrected with a calibration function that was made with the use of *N*,*N*'-dimethyl-3-nitroaniline and 4-dimethyl-4'-nitrostylbene as standard substances.²²

This work was financially supported by the Promotion and Mutual Aid Corporation for Private Schools of Japan through the Science Research Promotion Fund and through the High-tech Research Center project.

References

- D. R. McMillin and K. M. McNett, *Chem. Rev.*, 1998, **98**, 1201; D. R. McMillin, J. R. Kirchhoff and K. V. Goodwin, *Coord. Chem. Rev.*, 1985, **64**, 83; N. Armaroli, *Chem. Soc. Rev.*, 2001, **30**, 113.
- 2 J. R. Kirchoff, R. E. Gamache, Jr., M. W. Blaskie, A. D. Paggio, R. K. Lengeel and D. R. McMillin, *Inorg. Chem.*, 1983, **22**, 2380; M. T. Miller, P. K. Gantzel and T. B. Karpishin, *Angew. Chem., Int. Ed.*, 1998, **37**, 1556, and references therein.
- 3 M. K. Eggleston, D. R. McMillin, K. S. Koenig and A. J. Pallenbwrg, Inorg. Chem., 1997, 36, 172.
- 4 C. T. Cunningham, K. L. H. Cunningham, J. F. Michalec and D. R. McMillin, *Inorg. Chem.*, 1999, **38**, 4388; E. C. Reisgo, Y.-Z. Hu, F. Bouvier, R. P. Thummel, D. V. Scaltrito and G. J. Meyer, *Inorg. Chem.*, 2001, **40**, 3413; V. Kalsani, M. Schmittel, A. Listorti, G. Accorsi and Nicola Armaroli, *Inorg. Chem.*, 2006, **45**, 2061; D. Felder, J.-F. Nierengarten, F. Barigelletti, B. Ventura and N. Armaroli, *J. Am. Chem. Soc.*, 2001, **123**, 6291.
- R. A. Radet, D. R. McMillin, M. T. Buchner, T. G. Matthews, D. J. Casadonte, R. K. Lengel, S. B. Whitteaker, L. M. Darmon and F. E. Lytle, J. Am. Chem. Soc., 1981, 103, 5906; J. R. Kirchhoff, D. R. McMillin, W. R. Robinson, D. R. Powell, A. T. McKenzie and S. Chen, Inorg. Chem., 1985, 24, 3928; C. E. A. Palmer and D. R. McMillin, Inorg. Chem., 1987, 26, 3837; D. J. Casadonte, Jr. and D. R. McMillin, Inorg. Chem., 1987, 26, 3950; T. M. cCormick, W.-L. Jia and S. Wang, Inorg. Chem., 2006, 45, 147; S. E. Page, K. C. Gordon and A. K. Burrell, Inorg. Chem., 1998, 37, 4452; T. Tsubomura, N. Takahashi, K. Saito and T. Tsukuda, Chem. Lett., 2004, 33, 678; T. Tsukuda, A. Nakamura, T. Arai and T. Tsubomura, Bull. Chem. Soc. Jpn., 2006, 79, 288; N. Armaroli, G. Accorsi, M. Holler, O. Moudam, J.-F. Nierengarten, Z. Zhou, R. T. Wegh and R. Welter, Adv. Mater., 2006, 18, 1313.
- 6 S. Kuang, D. G. Cuttell, D. R. McMillin, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 2002, **41**, 3313; D. G. Cuttell, S.-M. Kuang,

- P. E. Fanwick, D. R. McMillin and R. A. Walton, J. Am. Chem. Soc., 2002, **124**, 7.
- 7 Seth B. Harkins and Jonas C. Peter, J. Am. Chem. Soc., 2005, **127**, 2030. 8 K. Saito, T. Tsukuda and T. Tsubomura, Bull. Chem. Soc. Inn. 2006.
- 8 K. Saito, T. Tsukuda and T. Tsubomura, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 437.
- 9 G. J. Kubas, Inorg. Synth., 1979, 19, 90.
- 10 P. Coppens, *Chem. Commun.*, 2003, 1317; P. Coppens, I. I. Vorontsov, T. Graber, A. Y. Kovalevsky, F. Chen, G. Wu, M. Gembicky and I. V. Novozhilova, *J. Am. Chem. Soc.*, 2004, **126**, 5980.
- E. W. Ainscough, E. N. Baker, A. G. Bingham, A. M. Brodie and C. A. Smith, *J. Chem. Soc. Dalton Trans.*, 1989, 2167; G. Doyle, K. A. Eriksen and D. V. Engen, *J. Am. Chem. Soc.*, 1985, **107**, 7914; A. P. Gaughan, R. F. Ziolo and Z. Dori, *Inorg. Chem.*, 1971, **10**, 2777; A. P. Gaughan, K. S. Bowman and Z. Dori, *Inorg. Chem.*, 1972, **11**, 601; B. Mohr, E. E. Brooks, N. Rath and E. Deutsch, *Inorg. Chem.*, 1991, **30**, 4541.
- 12 S. Kitagawa, M. Kondo, S. Kawata, S. Wada, M. Maekawa and M. Munakata, *Inorg. Chem.*, 1995, **34**, 1455; M. Bettenhousen, A. Eichhöfer, D. Fenske and M. Semmelman, *Z. Anorg. Allg. Chem.*, 1999, **625**, 593; P. Comba, C. Katsichtis, B. Nuber and H. Pritzkow, *Eur. J. Inorg. Chem.*, 1999, 777.
- 13 S. Sakaki, H. Mizutani, Y. Kase, K. Inokuchi, T. Arai and T. Hamada, J. Chem. Soc., Dalton Trans., 1996, 1909.
- 14 (a) CrystalClear, Area Detector Processing Software, Rigaku and Molecular Structure Corp., The Woodlands, TX, 2000; (b) J. W. Pflugrath, Acta Crystallogr., Sect. D, 1999, 55, 1718.
- 15 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori and M. Camalli, J. Appl. Crystallogr., 1994, 27, 435.
- 16 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, *The DIRDIF-99 program system*, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.
- 17 Crystal Structure, Crystal Structure Analysis Package, Rigaku and Molecular Structure Corp., The Woodlands, TX, 2000–2004.
- 18 G. M. Sheldrick, SHELXL97. Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- 19 teXsan, Crystal Structure Analysis Package, Ver. 2.0, Molecular Structure Corporation, The Woodlands, TX, 2004.
- 20 ORTEP-3 for Windows: L. J. Farrugia, J. Appl. Crystallogr., 1997, 30, 565.
- 21 Z. A. Siddique, T. Ohno, K. Nozaki and T. Tsubomura, *Inorg. Chem.*, 2004, **43**, 663.
- 22 E. Lippert, W. Nägele, I. Seibold-Blankenstein, U. Staiger and W. Voss, Z. Anal. Chem., 1959, 17, 1.