

The first heterothiometallic complex of bis(diphenylthiophosphoryl)-amide $[(\text{Ph}_2\text{PS})_2\text{N}]^-$: synthesis, crystal structure and nonlinear optical effects of the dodecanuclear cluster compound $(\text{Et}_4\text{N})_4[\text{Mo}_4\text{Cu}_8\text{O}_4\text{S}_{12}\{(\text{Ph}_2\text{PS})_2\text{N}\}_4]$

Yun-Yin Niu,^a Ying-Lin Song,^b He-Gen Zheng,^a De-Liang Long,^a Hoong-Kun Fun^c and Xin-Quan Xin^{*a}

^a State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China

^b Harbin Institute of Technology, Physical Department, Harbin 150001, P. R. China

^c X-Ray Crystallography Unit, School of Physics, Universiti Sains Malaysia 11800, USM, Penang, Malaysia

Received (in Montpellier, France) 8th March 2001, Accepted 25th April 2001

First published as an Advance Article on the web 8th June 2001

The heterothiometallic cluster compound $(\text{Et}_4\text{N})_4[\text{Mo}_4\text{Cu}_8\text{O}_4\text{S}_{12}\{(\text{Ph}_2\text{PS})_2\text{N}\}_4]$ has been synthesized by the reaction of $(\text{Et}_4\text{N})_2[\text{Mo}_2\text{Cu}_6\text{Br}_2\text{I}_4\text{O}_2\text{S}_6]$ with $\text{K}[(\text{Ph}_2\text{PS})_2\text{N}]$ in CH_3CN . An X-ray structure determination revealed that the anionic cluster consists of a square $[\text{Mo}_4\text{Cu}_4\text{O}_4\text{S}_{12}]^-$ framework which is formed by four MoOS_3^{2-} building blocks linked *via* four Cu atoms, and four pendant $\text{Cu}[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]$ units, each bound to one of the corner MoOS_3 moieties. The structure can also be regarded as a tetramer of nest-shaped $\text{MoCu}_3\text{OS}_3[(\text{Ph}_2\text{PS})_2\text{N}]$ monomers co-polymerized by sharing the limbic Cu atoms. The $[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ ligand adopts a classical S,S' -chelating mode, resulting in the formation of a six-membered $\text{CuS}_2\text{P}_2\text{N}$ ring of chair configuration. The nonlinear optical (NLO) properties were studied with an 8 ns pulsed laser at 532 nm. Its optical response to the incident light exhibits good optical absorptive and refractive effects, with $\alpha_2 = 1.2 \times 10^{-11} \text{ m W}^{-1}$ and $n_2 = -2.04 \times 10^{-18} \text{ m}^2 \text{ W}^{-1}$ for a $1.2 \times 10^{-4} \text{ mol dm}^{-3}$ DMF solution.

The coordination chemistry of thiometallates $[\text{MO}_n\text{S}_{4-n}]^{2-}$ ($\text{M} = \text{Mo}, \text{W}; n = 0-2$) and their related compounds has been well documented owing to their relevance to certain biological processes,^{1,2} catalytic reactions³ and their strong nonlinear optical characteristics.⁴ To date, some of us have reported a number of new nonlinear optical materials based on clusters with different structural modes, including the supra-cubic cage,⁵ twin-nest shape,⁶ incomplete cubane,^{7,8} hexagonal prism shape⁹ and windmill-like structure.^{10,11} Unfortunately, direct technical applications are often frustrated by the clusters' low solubility in common organic solvents. One way to circumvent this practical problem is to introduce bulky organic ligands into the clusters to increase their solubility. The bis(dialkylchalcogenidophosphoryl)amide $[(\text{R}_2\text{PQ})_2\text{N}]^-$ ($\text{Q} = \text{S}$ or Se ; $\text{R} = \text{Ph}$ or Pr) ligands were selected for this purpose. Although they have recently been the focus of many studies due to the structural diversity of their metal complexes,¹²⁻¹⁹ there are few examples of their complexes with reactive cluster units. In this paper we describe the single crystal X-ray structure of a remarkable square-like dodecanuclear cluster compound synthesized by a two-step solid-liquid strategy. Investigation of the cluster's nonlinear optical properties showed that it exhibits good nonlinear absorptive and refractive properties.

Experimental

Materials and general methods

The compound $(\text{NH}_4)_2[\text{MoO}_2\text{S}_2]$ was prepared by the literature method.²⁰ $\text{K}[(\text{Ph}_2\text{PS})_2\text{N}]$ was obtained from the reaction of $(\text{Ph}_2\text{PS})_2\text{NH}$ with KOBu^t in MeOH in an analogous manner to literature procedures.^{21,22} Solvents and the solid

reagents were purchased as AR grade and used without further purification. Infrared spectra were recorded on a Fourier FT-10SX spectrophotometer from pressed KBr pellets. Electronic spectra were taken on a Hitachi U-3410 spectrophotometer. Carbon and hydrogen analyses were obtained on a PE 240C elemental analyzer. The compositions of copper and molybdenum were analyzed with a JA 1100 + 2000 ICP quantometer.

Synthesis of $(\text{Et}_4\text{N})_4[\text{Mo}_4\text{Cu}_8\text{O}_4\text{S}_{12}\{(\text{Ph}_2\text{PS})_2\text{N}\}_4]$. A well-ground mixture of $(\text{NH}_4)_2[\text{MoO}_2\text{S}_2]$ (0.23 g, 1 mmol), CuI (0.40 g, 2 mmol) and Et_4NBr (0.42 g, 2 mmol) was put into a reaction tube and heated at 80°C for 4 h under a nitrogen atmosphere. After extracting the resultant black solid with CH_3CN (30 mL), the extract was filtered to afford a deep-red filtrate.⁶ Block-shaped dark-red crystals of the title compound were obtained by adding a solution of $\text{K}[(\text{Ph}_2\text{PS})_2\text{N}]$ (0.49 g, 1 mmol) in 5 mL CH_3CN (one drop of water was added to increase the solubility of the potassium salt) into the filtrate and allowing it to stand for 2 days. Yield 0.26 g, 28% based on Mo. The product shows characteristic infrared absorptions (KBr pellet, cm^{-1}): $\nu(\text{P}_2\text{N})$ 1172(s) and 787(s); $\nu(\text{P}-\text{S})$ 576(vs), $\nu(\text{Mo}-\text{O})$ 903(vs), $\nu(\text{Mo}-\text{S}_b)$ 445(s). Anal. calc. for $\text{C}_{128}\text{H}_{160}\text{Cu}_8\text{Mo}_4\text{N}_8\text{O}_4\text{P}_8\text{S}_{20}$: C, 42.05; H, 4.41; N, 3.06; Cu, 13.91; Mo, 10.49; found: C, 42.10; H, 4.45; N, 3.17; Cu, 13.60; Mo, 10.90%.

Crystallography

A deep-red prismatic crystal was mounted on a glass fiber. All measurements were carried out on a Siemens Smart CCD area detector diffractometer by using an ω -scan technique. The data reductions were performed on a Silicon Graphics

Table 1 X-Ray crystallographic data for $(\text{Et}_4\text{N})_4[\text{Mo}_4\text{Cu}_8\text{O}_4\text{S}_{12}\{(\text{Ph}_2\text{PS})_2\text{N}\}_4]$

Chemical formula	$\text{C}_{128}\text{H}_{160}\text{Cu}_8\text{Mo}_4\text{N}_8\text{O}_4\text{P}_8\text{S}_{20}$
Formula weight	3655.68
Crystal system	Tetragonal
Space group	$I4_1/a$
$a/\text{\AA}$	29.1337(2)
$b/\text{\AA}$	29.1337(2)
$c/\text{\AA}$	19.7246(2)
$U/\text{\AA}^3$	16 741.7(2)
Z	16
$\lambda(\text{Mo-K}\alpha)/\text{\AA}$	0.710 73
μ/mm^{-1}	1.654
$R, wR [I > 2\sigma(I)]$	0.0554, 0.1287
(all data)	0.1251, 0.1595

Indy workstation using Smart CCD software and an empirical SADABS absorption correction was applied.²³ The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-PC (Version 5.1) package.²⁴ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in their calculated positions (C–H 0.96 Å), assigned fixed isotropic thermal parameters (1.2 times for CH_2 and 1.5 times for CH_3 of the atoms to which they are attached) and allowed to ride on their respective parent atoms. Their contributions were included in the structure factor calculations. Table 1 shows the details of data processing and structure refinements.

CCDC reference number 156519. See <http://www.rsc.org/suppdata/nj/b1/b102238p/> for crystallographic data in CIF or other electronic format.

Optical measurements

A DMF solution of the compound was placed in a 5 mm quartz cuvette for NLO measurements and the NLO properties were measured with an 8 ns pulse at 532 nm generated from a Q-switched frequency-doubled Nd : YAG laser. The spatial profiles of the optical pulses were nearly Gaussian after passage through a filter. The pulsed laser was focused onto the sample cell with a 15 cm focal length lens. The spot radius of the laser beam was measured to be 55 μm . Incident and transmitted pulse energies were measured simultaneously by two energy detectors (RJP-735 Energy Probes, laser precision). The NLO properties of the sample were determined by performing z -scan measurements. The sample was mounted on a translation stage that was controlled by a computer to move along the z axis with respect to the focal point. An aperture of 0.5 mm radius was placed in front of the transmission detector and the transmittance was recorded as a function of the sample position on the z axis (closed aperture z -scan). To obtain the NLO absorption, the z -dependent sample transmittance was measured without the aperture (open aperture z -scan).

Results and discussion

Synthesis and characterization

Clusters with an open square-like framework have aroused great interest for their aesthetic symmetry^{25–31} and large optical limiting properties.³² Interestingly, they can also act as good building blocks for polymerization.^{26,33–36} In contrast to the wealth of pentanuclear square frameworks,^{25–36} there are remarkably few examples of the title type reported.³⁷ Twin nest-shaped products are of interest because their bridge cleavage can introduce different ligands into the cluster structure with the substituted products often maintaining the nest-shaped skeleton.³⁸ Taking advantage of this reactivity, we firstly succeeded in introducing $[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ into the

heterothiometallate system through ligand replacement in two steps: (1) preparation of a solution containing the reactive twin nest-shaped dimer $(\text{Et}_4\text{N})_2[\text{Mo}_2\text{Cu}_6\text{Br}_2\text{I}_4\text{O}_2\text{S}_6]$ by a solid state reaction below 100 °C, according to our previous work;^{4,6} and (2) reaction of the dimer with $[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ in acetonitrile followed by crystal growth from solution. The second step probably comprises a substitution reaction and an oligomerization process together with the elimination of a CuI species (Scheme 1). This procedure was based on the principle that solid–liquid reactions at low heating temperature possess characteristic properties similar to those of the original solid–gas reactions.³⁹ This was later substantiated by the failure of attempts to produce a tungsten analog of $(\text{Et}_4\text{N})_4[\text{Mo}_4\text{Cu}_8\text{O}_4\text{S}_{12}\{(\text{Ph}_2\text{PS})_2\text{N}\}_4]$ by the same method using $(\text{NH}_4)_2[\text{WO}_2\text{S}_2]$ as the starting material; in this system the corresponding twin nest-shaped tungsten analog has never been isolated.^{4,6}

The structure of $(\text{Et}_4\text{N})_4[\text{Mo}_4\text{Cu}_8\text{O}_4\text{S}_{12}\{(\text{Ph}_2\text{PS})_2\text{N}\}_4]$ has been determined by single crystal X-ray diffraction, the asymmetric unit being one-quarter of the formula unit. The anionic cluster core is shown in Fig. 1. Selected bond distances and angles are listed in Table 2. The cluster nucleus consists of four corner Mo atoms and four edge Cu (Cu2) atoms in an approximately square array, together with four capping Cu atoms (Cu1) each attached to a corner Mo atom. The cluster anion in the crystal is located at the -4 site with four Mo atoms at the corners of a distorted square of edge length 5.48

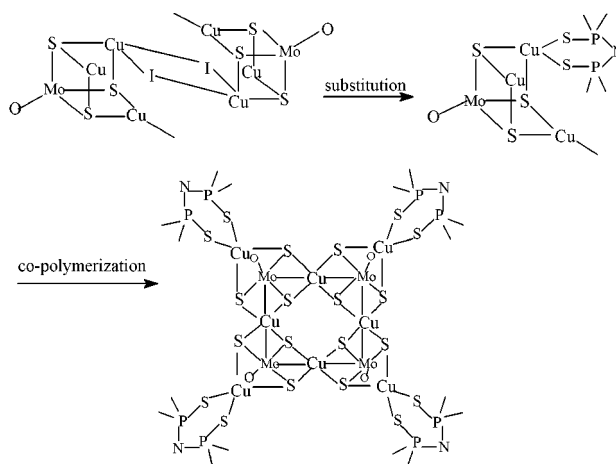
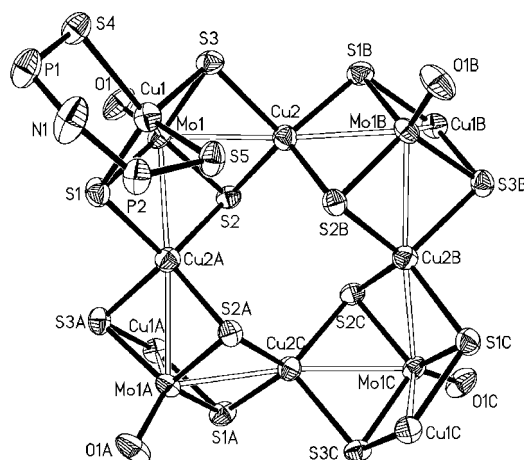
**Scheme 1** Substitution and co-polymerization of the twin-nest intermediate in CH_3CN solution.**Fig. 1** ORTEP diagram (30% probability ellipsoids) showing the cluster core of the title compound. Only one six-membered $\text{CuS}_2\text{P}_2\text{N}$ ring is shown for clarity. Symmetry code: (A) $+y, -x, 1-z$; (B) $-y, +x, 1-z$; (C) $1-x, -y, z$.

Table 2 Selected bond lengths (Å) and angles (°) in (Et₄N)₄[Mo₄Cu₈O₄S₁₂{(Ph₂PS)₂N}₄]

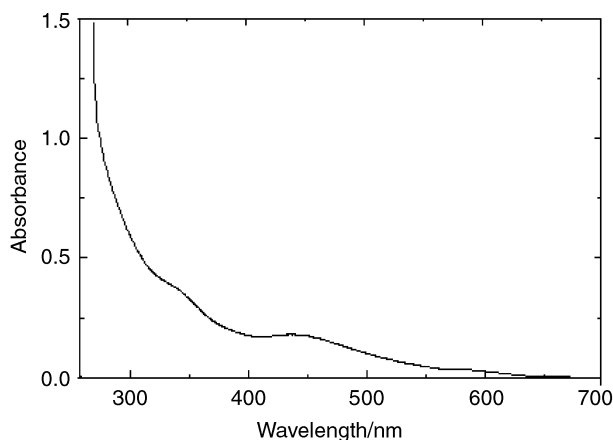
Mo1–O1	1.703(3)	Mo1–S3	2.2481(13)
Mo1–S2	2.2493(12)	Mo1–S1	2.2623(15)
Mo1–Cu1	2.7314(7)	Mo1–Cu2A	2.7359(7)
Mo1–Cu2	2.7719(7)	Cu1–S3	2.2853(14)
Cu1–S1	2.2870(14)	Cu1–S5	2.3251(15)
Cu1–S4	2.3664(14)	Cu2–S1B	2.3006(14)
Cu2–S2	2.3181(14)	Cu2–S2B	2.3473(14)
Cu2–S3	2.3657(13)		
O1–Mo1–S3	111.03(15)	O1–Mo1–S2	110.60(14)
S3–Mo1–S2	108.26(5)	O1–Mo1–S1	110.85(16)
S3–Mo1–S1	107.09(5)	S2–Mo1–S1	108.89(5)
S3–Cu1–S5	111.53(5)	S3–Cu1–S1	105.01(5)
S3–Cu1–S4	100.79(5)	S1–Cu1–S5	116.35(6)
S5–Cu1–S4	107.31(5)	S1–Cu1–S4	114.77(5)
S1B–Cu2–S2B	104.31(5)	S1B–Cu2–S2	124.60(6)
S1B–Cu2–S3	99.87(5)	S2–Cu2–S2B	109.18(6)
S2B–Cu2–S3	117.30(5)	S2–Cu2–S3	102.17(5)
Mo1–S1–Cu1	73.80(4)	Mo1–S1–Cu2A	73.67(4)
Mo1–S2–Cu2A	73.02(4)	Mo1–S2–Cu2	74.71(4)
Cu1–S1–Cu2A	111.77(6)	Cu2–S2–Cu2A	104.13(5)
Mo1–S3–Cu1	74.10(4)	Mo1–S3–Cu2	73.80(4)
Cu1–S3–Cu2	102.86(5)	P1–S4–Cu1	102.85(7)
		P2–S5–Cu1	101.58(7)

Å (Mo···Mo). If the amide ligands are excluded, there exists two approximate mirror planes, which intersect at the -4 axis and individually involve the two diagonal directions of the square framework. The tetrahedron consisting of the corner MoOS₃ moieties is manifested in the S–Mo–S(O) angles that range from 107.0(9) to 111.0(3)°; each of the four edge Cu atoms displays highly distorted tetrahedral coordination to four μ_3 -S atoms with S–Cu–S angles ranging from 99.8(7) to 117.3(0)°. The four capping Cu atoms coordinated to the [Ph₂P(S)NP(S)Ph₂][−] ligand also display highly distorted tetrahedral coordination with S–Cu–S angles varying in the range 100.7(9)–116.3(5)°. Interestingly, the Mo–Cu distances are similar (2.73–2.77 Å), even though the two Cu atoms are in different coordination environments. The short Mo–Cu distances indicate significant cluster interactions between these heteronuclear metal atoms. Four capping Cu–S₂P₂N subunits are alternately located above and below the square framework plane as the MoOS₃ moieties change their orientations in the framework. Each CuS₂P₂N metallacycle adopts a familiar chair configuration, exhibiting shorter P–N [mean 1.58(3) Å] and longer P–S bonds [1.99(8) Å] than those found in the free [S₂P₂(Ph₄N)][−] salt, which is consistent with delocalization within the ring.² Another way to view the cluster core is in terms of the nest-shaped building block [MoOS₃Cu₃]⁺. Four such units in alternate orientations are co-polymerized by sharing four limbic Cu atoms to form the greater oligomeric motif (see Fig. 1).

Optical response

The UV-visible absorption spectrum of the cluster in DMF solution is shown in Fig. 2. Although two distinct absorption peaks were found at 340 and 440 nm, the cluster has relatively low linear absorption in the visible and near-IR region.

A z -scan measurement of the compound in a DMF solution (1.2×10^{-4} mol dm^{−3}) is shown in Fig. 3(a), where the filled squares are the experimental data measured with an open aperture. This clearly illustrates that the absorption increases as the incident light irradiance rises since light transmittance (T) is a function of the sample's z position (with respect to the focal point at $z = 0$). Nonlinear absorption [$\alpha = \alpha_2(I_i)$] and linear absorption (α_0) can be described well by eqn. (1) and (2), where α and α_0 are the linear and effective third-order NLO absorptive coefficients, respectively, τ is the time, and L is the optical path. The solid line is the theoretical curve from eqn.

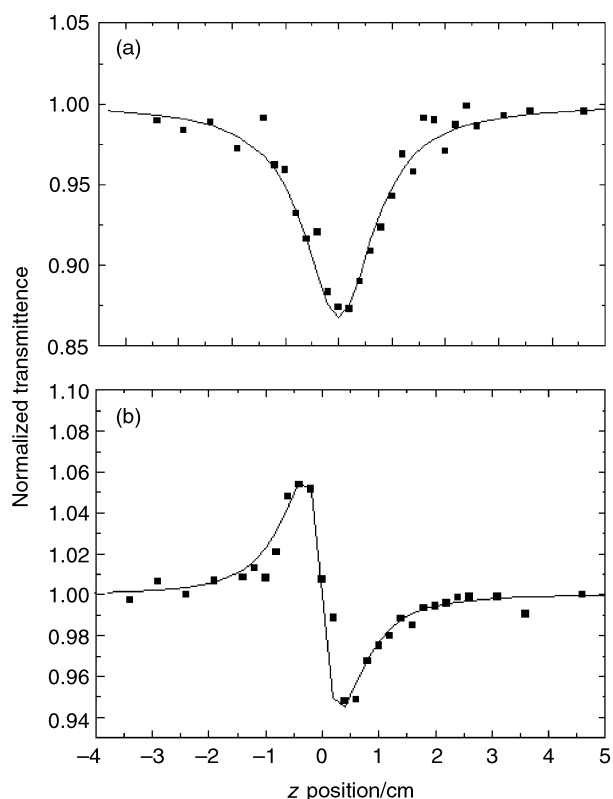
**Fig. 2** Absorption spectra of the title compound as a 1.2×10^{-4} mol dm^{−3} DMF solution with a 1 mm optical length.

(1) and (2)⁴⁰ and the effective nonlinear absorptive index, α_2 , is estimated to be 1.2×10^{-11} mW^{−1}.

$$T(z) = \frac{1}{\sqrt{\pi}q(z)} \int_{-\infty}^{\infty} \ln[1 + q(z)]e^{-\tau^2} d\tau \quad (1)$$

$$q(z) = \alpha_2^{\text{eff}} I(z) \frac{1 - e^{-\alpha_0 L}}{\alpha_0} \quad (2)$$

The nonlinear refractive components of the compound were assessed by dividing the normalized z -scan data obtained in the open aperture configuration [Fig. 3(b)]. An effective third-order nonlinear refractive index n_2 can be derived from the difference between normalized transmittance values at valley and peak positions (ΔT_{V-P}) by using eqn. (3). The data show that the cluster has a negative refractive nonlinearity, which

**Fig. 3** z -scan measurement of the title compound as a 1.2×10^{-4} mol dm^{−3} DMF solution. (a) The data were collected with an open aperture configuration. (b) The data were obtained by dividing the normalized z -scan measured with a closed aperture configuration by the normalized z -scan data in (a).

indicates self-defocusing behavior. The effective third-order NLO refractive index n_2 is given by:

$$n_2^{\text{eff}} = \frac{\lambda \alpha_0}{0.812\pi I(1 - e^{-\alpha_0 L})} \Delta T_{V-P} \quad (3)$$

where L is the sample thickness, I is the peak irradiation intensity at focus and λ is the wavelength of the laser. The refractive index n_2 was calculated to be $-2.04 \times 10^{-18} \text{ m}^2 \text{ W}^{-1}$. A good fit was found between theory and experiment, indicating that the process is effectively third order. Although these measured values of α_2 and n_2 were obtained with a $1.2 \times 10^{-4} \text{ mol dm}^{-3}$ solution of the title compound, they are comparable with many of the best known third-order materials in neat solid form, such as SiO_2 ($2 \times 10^{-20} \text{ m}^2 \text{ W}^{-1}$) and CdS ($2.5 \times 10^{-18} \text{ m}^2 \text{ W}^{-1}$)⁴¹ or $\text{SrLaGa}_3\text{O}_7$ ($11.1 \times 10^{-20} \text{ m}^2 \text{ W}^{-1}$) and $\text{Ca}_2\text{Ga}_2\text{SiO}_7$ ($6.5 \times 10^{-20} \text{ m}^2 \text{ W}^{-1}$).⁴² The origins of these good NLO properties can be attributed to the third-order bound-electronic effect, excited-state effect, two-photon absorption and nonlinear scattering.^{43,44} A much larger n_2 value may be expected with more concentrated solutions. Further work on the NLO mechanism is in progress.

Acknowledgements

We gratefully acknowledge the financial support of the National Science Foundation of China (no. 29631040), Foundation of Harbin Institute of Technology, the Malaysian Government and Universiti Sains Malaysia (research grant R&D no. 305/PFIZIK/610942). We also thank Dr Mark Glenny, School of Chemistry, Nottingham University, for helpful discussions.

References

- R. H. Holm and E. D. Simhon, *Molybdenum Enzymes*, Wiley, New York, 1985.
- R. H. Holm, *Adv. Inorg. Chem.*, 1992, **38**, 1.
- A. Bose and C. R. Saha, *J. Mol. Catal.*, 1989, **49**, 271.
- H. W. Hou, X. Q. Xin and S. Shi, *Coord. Chem. Rev.*, 1996, **153**, 25.
- J. G. Li, X. Q. Xin, Z. Y. Zhou and K. B. Yu, *J. Chem. Soc., Chem. Commun.*, 1991, 250.
- H. W. Hou, X. Q. Xin, J. Liu, M. Q. Chen and S. Shi, *J. Chem. Soc., Dalton Trans.*, 1994, 3211.
- Z. R. Chen, H. W. Hou, X. Q. Xin, K. B. Yu and S. Shi, *J. Phys. Chem.*, 1995, **99**, 8717.
- S. Shi, Z. R. Chen, H. W. Hou, X. Q. Xin and K. B. Yu, *Chem. Mater.*, 1995, **7**, 1519.
- G. Sankane, T. Shibahara, H. W. Hou, X. Q. Xin and S. Shi, *Inorg. Chem.*, 1995, **34**, 4785.
- H. G. Zheng, W. H. Leung, W. Tan, D. L. Long, W. Ji, J. T. Chen, F. B. Xin and X. Q. Xin, *J. Chem. Soc., Dalton Trans.*, 2000, 2145.
- Q. F. Zhang, S. S. S. Raj, M. C. Hong, R. Cao, H. K. Fun and X. Q. Xin, *Inorg. Chem. Commun.*, 1999, **2**, 272.
- M. S. Balakrishna, B. D. Santarsiero and R. G. Cavell, *Inorg. Chem.*, 1994, **33**, 3079.
- P. Bhattacharyya, A. M. Z. Slawin and M. B. Smith, *J. Chem. Soc., Dalton Trans.*, 1998, 2467.
- T. Q. Ly and J. D. Woollins, *Coord. Chem. Rev.*, 1998, **176**, 451.
- V. Béreau, C. G. Pernin and J. A. Ibers, *Inorg. Chem.*, 2000, **39**, 854.
- C. G. Pernin and J. A. Ibers, *Inorg. Chem.*, 2000, **39**, 1216.
- G. G. Talanova, K. B. Yatsimivskii, I. N. Kuraeva, A. Y. Nazarenko, I. M. Aladzhua, O. V. Bikhovskaya, I. V. Leont'Eva and R. M. Kalyanova, *J. Coord. Chem.*, 2000, **51**, 21.
- E. V. Garcia, M. J. Rosales-Hoz, H. Noth, I. Haiduc and C. Siwestru, *Inorg. Chem. Commun.*, 2000, **3**, 173.
- M. B. Smith and A. M. Z. Slawin, *Polyhedron*, 2000, **19**, 695.
- J. W. McDonald, G. D. Frieson, L. D. Rosenhein and W. E. New, *Inorg. Chim. Acta.*, 1983, **72**, 205.
- F. T. Wang, J. Najdzionek, K. L. Leneker, H. Wassermann and D. M. Braitsd, *Inorg. Synth. Metal-Org. Chem.*, 1978, **8**, 120.
- P. Bhattacharyya, J. Novosad, J. Phillips, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1995, 1607.
- G. M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Göttingen, Germany, 1997.
- G. M. Sheldrick, SHELXTL-PC (Version 5.10), Siemens Analytical Instruments, Inc., Madison, WI, 1997.
- S. Sarkar and S. B. S. Mishra, *Coord. Chem. Rev.*, 1984, **59**, 239.
- J. R. Nichololson, A. C. Flood, C. D. Garner and W. Clegg, *J. Chem. Soc., Chem. Commun.*, 1983, 1179.
- F. Secheresse, S. Rebernes, F. Robert and Y. Jeannin, *J. Chem. Soc., Dalton Trans.*, 1991, 2875.
- Q. F. Zhang, S. S. S. Raj, H. K. Fun and X. Q. Xin, *Chem. Lett.*, 1999, 494.
- A. Muller, E. Krickmoyer, H. Bogge and M. Penk, *Chimica*, 1989, **43**, 319.
- M. T. Pope, J. P. Lang, X. Q. Xin and K. B. Yu, *Chin. J. Chem.*, 1995, **13**, 40.
- J. P. Lang, W. Y. Zhou, X. Q. Xin and K. B. Yu, *J. Coord. Chem.*, 1993, **30**, 173.
- M. K. M. Low, H. W. Hou, H. G. Zheng, W. T. Wong, G. X. Jin, X. Q. Xin and W. Ji, *Chem. Commun.*, 1998, 505; H. G. Zheng, W. L. Tan, W. Ji, W. H. Leung, I. D. Williams, D. L. Long, J. S. Huang and X. Q. Xin, *Inorg. Chim. Acta*, 1999, **294**, 73; Y. L. Song, C. Zhang, X. L. Zhao, Y. X. Wang, G. Y. Fang, G. C. Jin, S. L. Qu, S. P. Wu, X. Q. Xin and H. G. Ye, *Chem. Lett.*, 2000, 1076.
- J. M. Manoli, C. Potvin, F. Secheresse and S. Marzak, *J. Chem. Soc., Chem. Commun.*, 1986, 1557.
- J. M. Manoli, C. Potvin, F. Secheresse and S. Marzak, *Inorg. Chim. Acta*, 1988, **150**, 257.
- Q. F. Zhang, W. H. Leung, X. Q. Xin and H. K. Fun, *Inorg. Chem.*, 2000, **39**, 417.
- C. Zhang, G. C. Jin, Y. Xu, H. K. Fun and X. Q. Xin, *Chem. Lett.*, 2000, 502; C. Zhang, Y. L. Song, Y. Xu, H. K. Fun, G. Y. Fang, Y. X. Wang and X. Q. Xin, *J. Chem. Soc., Dalton Trans.*, 2000, 2823.
- Q. Huang, X. Wu, Q. Wang, T. Sheng and J. Lu, *Inorg. Chem.*, 1996, **35**, 893.
- H. W. Hou, H. G. Ang, S. G. Ang, Y. T. Fan, M. K. M. Low, W. Ji and Y. W. Lee, *Inorg. Chim. Acta*, 2000, **299**, 147.
- J. P. Lang, X. Q. Xin and K. B. Yu, *J. Coord. Chem.*, 1994, **33**, 99.
- M. Sherk-Bahae, A. A. Said, T. H. Wei, D. J. Hagan and E. W. Van Stryland, *IEEE J. Quantum Electron.*, 1990, **26**, 760; M. Sherk-Bahae, A. A. Said and E. W. Van Stryland, *Opt. Lett.*, 1989, **14**, 955.
- J. L. Bredas, C. Adant, P. Tackx and A. Persoons, *Chem. Rev.*, 1994, **94**, 243.
- Z. Burshtein, Y. Kostoulas and H. M. Van Driel, *J. Opt. Soc. Am. B*, 1997, **14**, 2477.
- W. Ji, W. Xie, S. H. Tang and S. Shi, *Mater. Chem. Phys.*, 1995, **43**, 1.
- M. Sherk-Bahae, D. C. Hutching, D. J. Hagan and E. W. Van Stryland, *Phys. Rev. Lett.*, 1991, **65**, 96.