Construction and Structure of Coordination Polymers Based on Tetrahedral Cu_4OBr_6 Centres Linked by Pyrazine

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A model of 1D-, 2D-, and 3D-frameworks constructed of tetrahedral centres linked by rod-like ligands according to the regularities given by diamond and lonsdaleite lattices has been developed. The composition of the 3D-framework polymer is expressed by the formula $O_{chs}\, b_{[2chs-0.5(ch+cs)-hs]}\, t_{[c(h+s)+2hs]}$, where c, h, and s represent the numbers of the tetrahedral centres O in three different dimensions of the 3D-framework, b and t denote the relative amounts of bridging and terminal rod-like ligands, respectively. For related sheet and chain polymers the formulas $O_{ch}\, b_{[1.5ch-0.5c-h]}\, t_{[ch+c+2h]}$ and $O_c b_{[c-1]}\, t_{[2c+2]}$ have been derived, respectively. The formulas have been applied to a series of synthesized $Cu_4OBr_6(pyz)_p$ ($p = 2.25—3.95$) complexes in order to describe their structure. The complex with the value of $p = 3.17$ consists of chains comprising about 6 linked tetrahedral Cu_4OBr_6 centres. The values of $p = 3.04$ and 2.90 correspond to sheet structures with 9 and 16 linked centres, respectively. The structures of the complexes with $p = 2.41$ and 2.25 consist of 3D-frameworks. For the former complex 124 and for the latter one 503 linked tetrahedral Cu_4OBr_6 centres have been estimated.

Polymeric materials of copper complexes provide novel structures and geometries [1] which are of interest for their magnetic and electronic properties [2—5]. Pyrazine as a bridging ligand links a variety of copper coordination centres [6] to form polymeric copper complexes comprising one-dimensional chains, two-dimensional sheets or three-dimensional frameworks.

There are several polymers built up of tetrahedral copper(I) centres linked by pyrazine, an infinite chain [7], infinite sheets [8, 9] with hexanuclear copper(I) units of a chair-type cyclohexane-like structure, and an infinite 3D-framework with a diamond lattice [10, 11]. The tetranuclear $Cu_4OX_6L_4$ complexes [12, 13] contain tetrahedral centres Cu_4OX_6 based on a bridging central oxygen atom bound to four tetrahedrally arranged copper(II) atoms. Each copper(II) atom adopts in the same time the trigonal bipyramidal coordination with one terminal axial position occupied by ligand L. When the terminal axial positions are occupied by rod-like pyrazine ligands, then the linking of tetrahedral centres can occur under the formation of chains, sheets or 3D-frameworks as it is known for the above-mentioned tetrahedral pyrazine copper(I) complexes.

Recently, we have reported a series of Cu_4OBr_6-$(pyz)_p$ ($p = 2—4$) complexes in which the tetrahedral Cu_4OBr_6 centres are linked by pyrazine ligands to form oligomeric 1D-, 2D- or 3D-frameworks depending of the mole ratio of the Cu_4OBr_6 and pyrazine reactants [14]. Experimentally determined

relative amounts of bridging b and terminal t pyrazine ligands for these complexes showed good correlation with the straight line $b = -0.5t + 2$ which is related to a single tetrahedral centre and describes the construction of diamond-related [11] structures relatively. In this work a model of linking is presented which describes the construction of diamond-related structures exactly. The model is applied to the above-mentioned oligomeric $Cu_4OBr_6(pyz)_p$ ($p = 2—4$) complexes with the aim to find their dimensions and the number of the tetrahedral Cu_4OBr_6 centres linked by pyrazine.

EXPERIMENTAL

The complexes were prepared by reaction of the initial $Cu_4OBr_6(MeOH)_4$ complex with pyrazine in methanol—ether solution according to the procedure described elsewhere [14]. The composition of the complexes calculated from the analytical data is presented in Table 5.

Infrared spectra of the $Cu_4OBr_6(pyz)_p$ complexes were recorded with Philips Analytical PU 9800 FTIR and Nicolet Magna 750 spectrophotometers in Nujol mull and polyethylene matrix.

The bands of infrared spectra at $\tilde{\nu} = 484\ cm^{-1}$ and $459\ cm^{-1}$ for bridging and terminal pyrazine ligands, respectively, have been used for determination of relative amounts of bridging b and terminal t pyrazine ligands in the $Cu_4OBr_6(pyz)_p$ complexes [14]. The peak areas P_b and P_t were obtained by a baseline method

[15] and processed with Omnic software [16].

The relative amounts of the total pyrazine (p) in the Cu$_4$OBr$_6$(pyz)$_p$ complexes were calculated from the elemental analysis and those of bridging (b) and terminal (t) pyrazine (Table 5) using the equations

$$b + t = p \qquad (1)$$

$$(P_b/P_t) = (A_b/A_t)(b/t) \qquad (2)$$

$$(P_b/P_t) = (A_b/A_t)(2 - 0.5p)/(p - 2) \qquad (3)$$

$$b = -0.5t + 2 \qquad (4)$$

The ratio of the integrated absorption coefficients A_b/A_t was determined by means of eqn (3) which was derived using eqns (1), (2), and (4). It was found that the relative amounts of bridging and terminal pyrazine ligands in the Cu$_4$OBr$_6$(pyz)$_p$ complexes satisfy eqn (4) that was derived for the diamond-related structures [14].

A plot of P_b/P_t vs. $(2 - 0.5p)/(p - 2)$ presented in Fig. 1 shows a straight line $(P_b/P_t) = 0.580(2 - 0.5p)/(p - 2) + 0.004$ with the slope of $A_b/A_t = 0.580$ ($R^2 = 0.9984$) and a negligible deviation from the coordinate origin.

RESULTS AND DISCUSSION

The model of linking applied to the Cu$_4$OBr$_6$(pyz)$_p$ complexes is based on an idea that small (elemental) oligomeric structures (chains, sheets, and 3D-frameworks) grow attaching the coordination centres by linking rod-like ligands in arbitrary of the three dimensions to reach infinite structures according to the regularities which are determined by a given lattice.

A 3D-framework based on diamond or lonsdaleite lattices constructed of tetrahedral coordination centres by linking procedure can be described by three parameters, c, h, and s. Each of these parameters represents the number of the tetrahedral centres in three different dimensions of the 3D-framework.

The product chs gives the total number of tetrahedral centres in the 3D-framework. At the same time c signifies the number of tetrahedral centres in a chain, h is the number of the chains linked into a sheet, and s represents the number of the sheets stacked by linking into a 3D-framework. The total number of tetrahedral centres in the 3D-framework equals also the sum of external centres which are in the planes ch, cs, hs and internal centres which are placed inside the 3D-framework and their number is given by the product $(c - 2)(h - 2)(s - 2)$. While all internal tetrahedral centres are of the same linking mode L$_4$ (Ob_4), the external centres are represented by different linking modes L$_3$ (Ob_3t), L$_2$ (Ob_2t_2), and L$_1$ (Obt_3). These linking modes are ordered in the planes with a certain periodicity, which is driven by the lattice regularities and depends also on even and odd values of c, h, and s parameters. The numbers of the individual linking modes in the planes ch, cs, and hs as a function of c, h, and s parameters have been expressed for all combinations of even c_e, h_e, s_e and odd c_o, h_o, s_o values of c, h, and s parameters.

The expressions for the total sum of the individual linking modes for 3D-framework described by c, h, and s parameters are presented in Table 1.

The differences in the constructions of diamond and lonsdaleite lattices are termed submodifications S. While all combinations of even and odd values involving even values of parameter c_e give the same submodification S$_1$, the combinations involving odd values of parameter c_o produce different submodifications S$_1$, S$_2$, S$_3$, S$_4$, and S$_5$. However, the averaged numbers of

Table 1. Number of Linking Modes for 3D-Frameworks with Diamond or Lonsdaleite Lattices and c, h, and s Dimensions

Combination of even and odd c, h, s	Submodification S	Number of linking modes			
		L$_1$	L$_2$	L$_3$	L$_4$
$c_e - h_e - s_e$ $c_e - h_e - s_o$ $c_e - h_o - s_e$ $c_e - h_o - s_o$ $c_o - h_o - s_o$ $c_o - h_e - s_e{}^a$	S$_1$	2	$c + 2(h + s) - 6$	$c(h + s - 2) + 2(h - 2)(s - 2) - 2$	$chs - c(h + s - 1) - 2(h - 1)(s - 1)$
$c_o - h_o - s_e$	S$_2$	4	$c + 2(h + s) - 9$	$c(h + s - 2) + 2(h - 2)(s - 2) - 1$	$chs - c(h + s - 1) - 2(h - 1)(s - 1)$
$c_o - h_e - s_o{}^a$	S$_3$	0	$c + 2(h + s) - 3$	$c(h + s - 2) + 2(h - 2)(s - 2) - 3$	$chs - c(h + s - 1) - 2(h - 1)(s - 1)$
	(S$_2$ + S$_3$)/2	2	$c + 2(h + s) - 6$	$c(h + s - 2) + 2(h - 2)(s - 2) - 2$	$chs - c(h + s - 1) - 2(h - 1)(s - 1)$
$c_o - h_e - s_o{}^b$	S$_4$	4	$c + 2h + 4s - 11$	$c(h + s - 2) + 2(h - 2)(s - 2) - 3s + 2$	$chs - c(h + s - 1) + 2(h - hs) + 3s - 3$
$c_o - h_e - s_e{}^b$	S$_5$	0	$c + 2h - 1$	$c(h + s - 2) + 2(h - 2)(s - 2) + 3s - 6$	$chs - c(h + s - 1) + 2(h - hs) + s - 1$
	(S$_4$ + S$_5$)/2	2	$c + 2(h + s) - 6$	$c(h + s - 2) + 2(h - 2)(s - 2) - 2$	$chs - c(h + s - 1) - 2(h - 1)(s - 1)$

a) Valid only for diamond lattice. b) Valid only for lonsdaleite lattice.

Table 2. Number of Bridging and Terminal Ligands in Linking Modes for 3D-Framework of S_1-Submodification with Dimensions c, h, and s

Linking mode	Number of bridging ligands	Number of terminal ligands
L_1	0.5×2	3×2
L_2	$c + 2(h + s) - 6$	$2[c + 2(h + s) - 6]$
L_3	$1.5[c(h + s - 2) + 2(h - 2)(s - 2) - 2]$	$c(h + s - 2) + 2(h - 2)(s - 2) - 2$
L_4	$2[chs - c(h + s - 1) - 2(h - 1)(s - 1)]$	0
$L_1 + L_2 + L_3 + L_4$	$2chs - 0.5(ch + cs) - hs$	$c(h + s) + 2hs$

Table 3. Number of Bridging and Terminal Ligands for 3D-Frameworks of S_1—S_5-Submodifications with Dimensions c, h, and s

Submodification	Number of bridging ligands	Number of terminal ligands
S_1	$2chs - 0.5(ch + cs) - hs$	$c(h + s) + 2hs$
S_2	$2chs - 0.5(ch + cs) - hs - 0.5$	$c(h + s) + 2hs + 1$
S_3	$2chs - 0.5(ch + cs) - hs + 0.5$	$c(h + s) + 2hs - 1$
S_4	$2chs - 0.5(ch + cs) - hs - 0.5s$	$c(h + s) + 2hs + s$
S_5	$2chs - 0.5(ch + cs) - hs + 0.5s$	$c(h + s) + 2hs - s$

Table 4. Number of Bridging and Terminal Ligands for Sheet M_1—M_3-Modifications with Dimensions c and h

Modification	Number of bridging ligands	Number of terminal ligands
M_1	$1.5ch - 0.5c - h$	$c(h + 1) + 2h$
M_2	$1.5ch - 0.5c - h + 0.5$	$c(h + 1) + 2h - 1$
M_3	$1.5ch - 0.5c - h - 0.5$	$c(h + 1) + 2h + 1$

linking modes for the submodifications S_2 and S_3 as well as for S_4 and S_5 are the same as for the submodification S_1. If the submodifications S_2, S_3, S_4, and S_5 have the same weight in the linking procedure, then the linking characteristics of the submodification S_1 can be considered to have a nature of overall linking process and may be accepted for further calculations.

From the relations defining the number of the linking modes for 3D-framework of the submodification S_1 with dimensions c, h, and s and using the data of Table 2 the formula describing the composition of the oligomeric or infinite 3D-framework can be derived. By similar procedure the formulas for the submodifications S_2—S_5 can also be derived (Table 3).

When the number of the stacked sheets $s = 1$, the formula (5) is transformed to the expression (6), which describes the composition of the 2D-framework. The formula describing the composition of the 1D-framework (7) can be obtained when the number of the linked sheets $s = 1$ and the number of the linked chains $h = 1$.

$$O_{chs} \ b_{[2chs-0.5(ch+cs)-hs]} \ t_{[c(h+s)+2hs]} \quad (5)$$

$$O_{ch} \ b_{[1.5ch-0.5c-h]} \ t_{[ch+c+2h]} \quad (6)$$

$$O_c \ b_{[c-1]} \ t_{[2c+2]} \quad (7)$$

The 2D-structure derived for the diamond-related lattice (when $s = 1$) can exist in three modifications as shown in Table 4. Application of the procedure presented above for 3D-framework submodifications to the 2D-modifications gives the formula (6).

The tetrahedral Cu_4OBr_6 centres present in the structure of the polymeric $Cu_4OBr_6(pyz)_p$ complexes are indicated by a diagnostic band of the tetrahedral OCu_4 core vibration in the region 536—544 cm^{-1} [14] and by a diagnostic d—d band at about 11500 cm^{-1} and a shoulder at about 13000 cm^{-1} characterizing the trigonal bipyramidal coordination of copper(II) atoms [17]. The linking of the tetrahedral Cu_4OBr_6 centres by pyrazine to form polymeric structures of the $Cu_4OBr_6(pyz)_p$ complexes is indicated by the bands in infrared spectra at 484 cm^{-1} and 459 cm^{-1} for bridging and terminal pyrazine ligands, respectively [14]. The absorbances of these bands vary with the extent of linking pyrazine. They have been used for determination of the relative amounts of bridging and terminal pyrazine ligands and the subsequent indirect structural characterization of the $Cu_4OBr_6(pyz)_p$ complexes as those having diamond-related lattice. The procedure of the bridging and terminal pyrazine ligand determination based on absorbances has been corrected by taking the relevant peak areas. The ratio of the integrated absorption coefficients obtained graphically using peak areas has been found to be
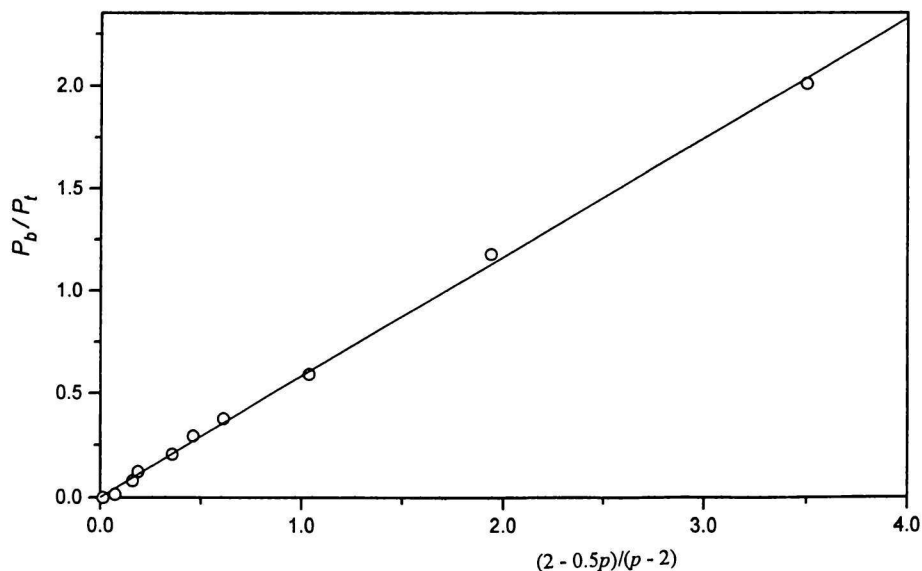
Fig. 1. Plot of P_b/P_t vs. $(2 - 0.5p)/(p - 2)$ for determination of integrated absorption coefficient ratio $A_b/A_t = 0.508$.

Table 5. Peak Area (P), Relative Amounts of Total (p), Bridging (b), Terminal (t) Pyrazine, and Wavenumbers of Cu_4O Core Vibration for $Cu_4OBr_6(pyz)_p$ Complexes

Complex	Composition	P_b/cm^{-1}	P_t/cm^{-1}	p	b	t	$\bar{\nu}(Cu_4O)$/cm^{-1}
I	$Cu_4OBr_6(pyz)_{3.95}$	0	3.238	3.95	0	3.95	536
II	$Cu_4OBr_6(pyz)_{3.75}$	0.063	3.875	3.75	0.11	3.64	536
III	$Cu_4OBr_6(pyz)_{3.52}$	0.066	0.821	3.52	0.43	3.09	536
IV	$Cu_4OBr_6(pyz)_{3.46}$	0.595	4.840	3.46	0.59	2.87	536
V	$Cu_4OBr_6(pyz)_{3.17}$	0.392	1.906	3.17	0.83	2.34	536
VI	$Cu_4OBr_6(pyz)_{3.04}$	0.670	2.275	3.04	1.01	2.03	538
VII	$Cu_4OBr_6(pyz)_{2.90}$	0.832	2.202	2.90	1.13	1.77	538
VIII	$Cu_4OBr_6(pyz)_{2.65}$	0.794	1.341	2.65	1.34	1.31	540
IX	$Cu_4OBr_6(pyz)_{2.41}$	1.043	0.885	2.41	1.60	0.81	544
X	$Cu_4OBr_6(pyz)_{2.25}$	0.191	0.095	2.25	1.75	0.50	544

$A_b/A_t = 0.580$ (Fig. 1). This value is higher than the previously used molar absorption coefficient ratio $\varepsilon_b/\varepsilon_t = 0.483$ which was calculated for approximately dimeric $Cu_4OBr_6(pyz)_{3.52}$ complex [14].

The number of the terahedral Cu_4OBr_6 centres linked by pyrazine in the chain oligomer, c, can be directly calculated using the one-parameter formula (7). It can be expected that the oligomer growth is controlled by the diamond lattice and none of the three dimensions is preferred. Therefore, the transformation of the three-parameter expression (5) to one-parameter formula of the cube is justified ($c = h = s = e$). Similarly, the expression (6) generally derived for 2D-frameworks can be transformed for square sheet when $c = h = d$. Then, the number of the terahedral Cu_4OBr_6 centres linked by pyrazine in the chain (parameter c), square sheet (parameter d), and cubic 3D-framework (parameter e) can be calculated by eqns (8), (9), and (10), respectively.

$$(b/t)_c = (c - 1)/(2c + 2) \qquad (b/t)_c \langle 1/6; 1/2 \rangle \quad (8)$$

$$(b/t)_d = [1.5d(d - 1)]/[d(d + 3)] \quad (b/t)_d \langle 3/10; 3/2 \rangle \quad (9)$$

$$(b/t)_e = [2e^2(e - 1)]/4e^2 \qquad (b/t)_e \langle 8/16; \infty \rangle \quad (10)$$

The limiting values of the b/t ratio are determined by the composition of the infinitive diamond-related 3D-, 2D-, and 1D-structures as well as by those of the related smallest 3D-, 2D-, and 1D-structural elements. From these limiting b/t data it follows that some of the b/t values describe the composition of the $Cu_4OBr_6(pyz)_p$ complexes with different structural dimensions, e.g. the interval of the b/t values for 2D-frameworks is partially coincident with those of 1D- or 3D-frameworks. Then, only the noncoincident b/t values provide the unambiguous dimensions of the oligomers.

The Cu_4O core vibration is slightly affected by the structural dimensions of the $Cu_4OBr_6(pyz)_p$ complexes. For the structurally different oligomers the slightly different but regular changes of the Cu_4O core vibration wavenumbers have been repeatedly ob-

Table 6. Estimated Structure and Number of Tetrahedral Cu_4OBr_6 Centres Linked by Pyrazine for Oligomers of $Cu_4OBr_6(pyz)_p$ Complexes

Complex	b/t	Number of linked centres	Number of linking modes				Structure of oligomer
			L_1	L_2	L_3	L_4	
III	0.1406	2	2	–	–	–	Chain
IV	0.2078	2.5	2	0.5	–	–	Chain
V	0.3545	6	2	4	–	–	Chain
VI	0.4957	9	2	5	2	–	Sheet
VII	0.6397	16	2	8	6	–	Sheet
VIII^a	1.0265	94	2	25	67	–	Sheet
		28	2	9	13	4	3D-Framework
IX	1.9936	124	2	19	56	47	3D-Framework
X	3.4762	503	2	34	179	88	3D-Framework

a) Estimated either for sheet or 3D-framework oligomers.

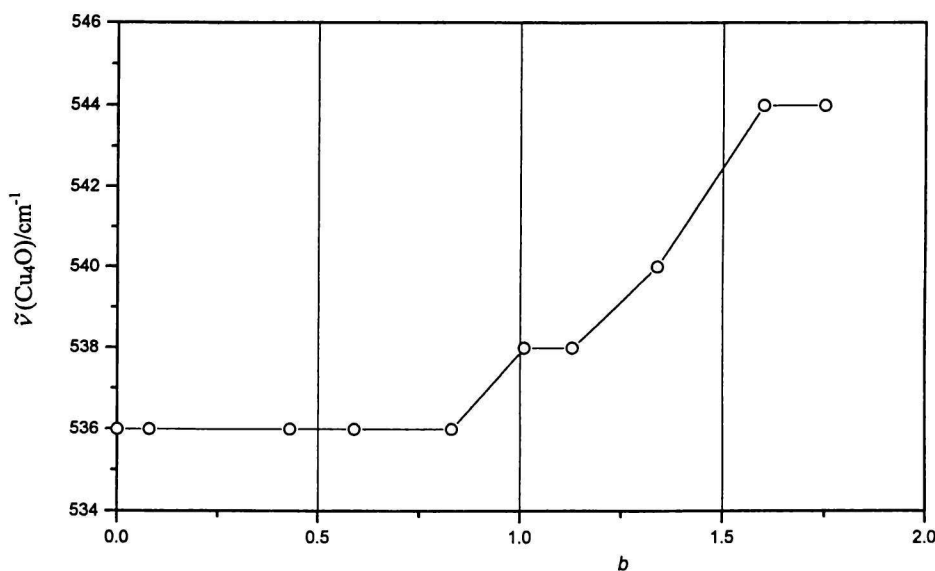**Fig. 2.** Relationship between wavenumbers of the Cu_4O core vibration and the relative amount of bridging pyrazine, b, in $Cu_4OBr_6(pyz)_p$ oligomers.

served. The plot of the wavenumbers *vs.* the amount of the bridging pyrazine ligand b in the $Cu_4OBr_6(pyz)_p$ complexes shows (Table 5, Fig. 2) the constant values at $\tilde{\nu} = 536$ cm^{-1} for the complexes *I—V* (chain oligomers, $b = 0$—1.00), at $\tilde{\nu} = 538$ cm^{-1} for the complexes *VI, VII* (sheet oligomers, $b = 1.00$—1.50), and at $\tilde{\nu} = 544$ cm^{-1} for the complexes *IX* and *X* (3D-oligomers, $b = 1.50$—2.00). However, for the complex *VIII* in the sheet oligomer region the wavenumber of the Cu_4O core vibration $\tilde{\nu} = 540$ cm^{-1} has been observed. The structure of this oligomer consists probably of both 2D- and 3D-frameworks. Generally, the data in Fig. 2 indicate a consecutive structural formation of the oligomers. The $Cu_4OBr_6(pyz)_p$ complexes can be structurally characterized as oligomers with the estimated oligomeric dimensions as presented in Table 6.

Supplementary material available. Supplementary material on periodicity of the linking modes is deposited with the authors.

REFERENCES

1. Hathaway, B. J., in *Comprehensive Coordination Chemistry*, Vol. *15*, p. 533. (Wilkinson, G., Editor.) Pergamon Press, London, 1988.
2. Eckberg, R. P. and Hatfield, W. E., *J. Chem. Soc., Dalton Trans. 1975*, 616.
3. Brown, D. B., Hall, J. W., Helis, H. M., Walton, E. G., Hodgson, D. J., and Hatfield, W. E., *Inorg. Chem. 16*, 2675 (1977).
4. Dariet, J., Haddad, M. S., Duesler, E. N., and Hendrickson, D. N., *Inorg. Chem. 18*, 2679 (1979).

5. Julve, M., De Munno, G., Bruno, G., and Verdaguer, M., *Inorg. Chem. 27*, 3160 (1988).
6. Steel, P. J., *Coord. Chem. Rev. 106,* 221 (1990).
7. Otieno, T., Rettig, S. J., Thompson, R. C., and Trotter, J., *Can. J. Chem. 67*, 1964 (1989).
8. Kitagawa, S., Munakata, M., and Tanimura, T., *Inorg. Chem. 31*, 1714 (1992).
9. Halasyamani, P., Heier, K. R., Willis, M. J., and Stern, Ch. L., *Z. Anorg. Allg. Chem. 622*, 479 (1996).
10. Otieno, T., Rettig, S. J., Thompson, R. C., and Trotter, J., *Inorg. Chem. 32*, 1607 (1993).
11. Hoskins, B. F. and Robson, R., *J. Am. Chem. Soc. 112*, 1546 (1990).
12. Bertrand, J. A. and Kelley, J. A., *J. Am. Chem. Soc. 88*, 4746 (1966).
13. Jorík, V., Koman, M., Makáňová, D., Mikloš, D., Broškovičová, A., and Ondrejovič, G., *Polyhedron 15*, 3129 (1996).
14. Broškovičová, A. and Ondrejovič, G., *Chem. Papers 52*, 16 (1998).
15. Horák, M. and Vítek, A., *Zpracování a interpretace vibračních spekter.* (Processing and Interpretation of Infrared Spectra.) P. 269. Nakladatelství technické literatury (Publishers of Technical Literature), Prague, 1980.
16. OMNIC, FTIR Software, Nicolet Analytical Instruments, Madison WI 53711, 1994.
17. tom Dieck, H., *Inorg. Chim. Acta 7*, 397 (1973).