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Electronic Spectra, ESR and Crystal Structure of Tetrahedral Halocuprates(II). The Existence of Cations (2tbpo·H$^+$) with a Very Short Hydrogen Bond

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Two compounds $[2tbpo\cdot H^+)_2[CuCl_4]^=$ *(yellow) and* $(2tbpo\cdot H^+)_2[CuBr_4]^=$ *(dark purple) (tbpo =tribenzylphosphine oxide) have been prepared and investigated by means of crystal structure, electronic, vibrational and ESR spectra. The crystal structure of the* $(2tbpo\cdot H^+)_2[CuCl_4]^=$ *complex was determined by three-dimensional X-ray diffraction. The compound crystallizes in the space group* $P4_2/n$ *with unit-cell dimensions* a = *19.585(2),* c = *9.883(1)*Å, V = *3790 (1)*Å^3, Z = *2,* D_m = *1.303 (flotation)* D_x = *1.302 Mg* m^{-3}. *The structure was solved by direct methods and refined by blocked full-matrix least-squares to* R = *0.053 for 2583 observed reflections. Cu(II) is coordinated to four chlorides in a tetrahedral arrangement. Tribenzylphosphine oxide molecules, related by a centre of inversion, are connected by a short hydrogen bridge. Chemical analysis, electronic and vibrational spectra showed that the bromide compound is similar to the chloride one and can be formulated as* $(2tbpo\cdot H^+)_2[CuBr_4]^=$. *The position of the* d–d *transition bands, the charge transfer bands, the ESR and the vibrational spectra of both complexes are discussed. The results are compared with analogous complexes cited in the literature.*

Introduction

Phosphine oxide complexes with transition metal ions have been studied extensively in the last twenty years. Among the phosphine oxides, tppo (triphenylphosphine oxide) was the ligand most used (see for example ref. 1 and references cited therein).

$CuCl_2$ and $CuBr_2$ form, with several phosphine oxides, complexes of the type $[CuX_2L_2]$; $[CuCl_2(tppo)_2]$ and $[CuBr_2(tppo)_2]$ have distorted tetrahedral structures [2, 3].

Our attempts to obtain analogous solid complexes with tbpo (tribenzylphosphine oxide) failed. On the presence of HCl or HBr, solid complexes involving tetrahedral $[CuX_4]^{2-}$ anions and (2tbpo·H$^+$) cations were obtained.

The halocuprate(II) anions have been investigated extensively since they assume various geometries, ranging from square planar through tetrahedral and on to trigonal bipyramidal [4]. Complexes with organic cations like N-phenylpiperazinium [5], N-methylpiperidinium, N,N'-dimethylpiperazinium [6], $CH_3NH_3^+$, $C_2H_5NH_3^+$, $(CH_3)_2NH_2^+$, $(CH_3)_2CHNH_3^+$, $(CH_3)_4N^+$ [7], N-methylphenethylammonium [8], N-benzylpiperazinium [9], glyH$_2^+$ and β-alaH$_2^+$ [10] were described.

Phosphonium cations have not yet been described in the literature, but $Hg_2Br_6^{2-}(2Ph_3AsO\cdot H^+)_2$ was reported by Harris, Inglis and McKechnie [11].

Experimental

tbpo was prepared by a Grignard reaction starting with benzylchloride and PBr_3 [12]; $CuCl_2$ was used as the hydrated salt $CuCl_2\cdot 2H_2O$ and $CuBr_2$ was freshly prepared in ethanolic solution starting with $CuCO_3\cdot Cu(OH)_2\cdot nH_2O$ and HBr 48%.

Preparation of the complexes

$(2tbpo\cdot H^+)_2[CuCl_4]^=$ was obtained by mixing hot ethanolic solutions of tbpo and $CuCl_2$ in a stoichiometric ratio of 2:1. Yellow crystals were precipitated instantaneously by adding a few drops of concentrated hydrochloride solution. The complex was recrystallized from ethanol. M.P. 176–182 °C.

$(2tbpo\cdot H^+)_2[CuBr_4]^=$ was obtained directly as dark purple crystals by adding benzene to the ethanolic mixture, even without addition of HBr. Ethanol and benzene were the solvents used in the recrystallization. M.P. 206–210 °C.

Analysis

The compounds were analyzed for carbon, hydrogen (microanalysis), copper(II), chloride and bromide. The solid complexes were dissolved in hot ethanol and decomposed with hot water. The insoluble ligand was separated by filtration. Copper(II) and

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the halides were determined in the solution by using EDTA and $AgNO_3$ respectively.

Anal. Calcd. for $(2tbpo{\cdot}H^+)_2[CuCl_4]^=$: C, 67.76; H, 5.78; Cu(II), 4.27; Cl, 9.53. Found: C, 67.4; H, 5.87; Cu(II), 4.29; Cl, 9.53%.

Anal. Calcd. for $(2tbpo{\cdot}H^+)_2[CuBr_4]^=$: C, 60.52; H, 5.16; Cu(II), 3.81; Br, 19.2. Found: C, 60.5; H, 5.32; Cu(II), 3.88; Br, 18.9%.

Physical Measurements

Electronic spectra of the solid complexes were obtained at room temperature over a 2000–350 nm range on a Cary Model 17 spectrophotometer using fluorolube mulls and quartz cells.

The infrared spectra of KBr or CsI pellets (4000–200 cm^{-1}) or nujol mulls were recorded on a Perkin-Elmer 567 spectrophotometer.

The ESR spectra were recorded on a Varian Model E-109 System Spectrometer.

Quartz sample tubes were employed for polycrystalline samples. Spectra were calibrated with diphenylpicrylhydrazyl (DPPH, g = 2.0036) as a field marker.

Crystal data collection - $[(C_{21}H_{21}PO)_2H^+]_2[CuCl_4]^=$ tetragonal, $P4_2/n$, $a = 19.585(2)$, $c = 9.883(1)$ Å, $V = 3790(1)$Å, $Z = 2$, $D_m = 1.301$ (flotation), $D_x = 1.302$ $Mg{\cdot}m^{-3}$.

A crystal with dimensions of 0.2 × 0.3 × 0.15 mm was mounted at random on an automatic CAD-4 diffractometer. Cell dimensions were determined by a least squares fit of settings for 25 reflections (±hkl). Intensity measurements were carried out up to $\theta = 75°$ using the $\omega/2\theta$ scan mode and graphite-monochromated CuKα radiation. 3625 unique reflections were measured, of which 2583 were considered observed $[|F| > 6\sigma(|F|)]$ and retained for use in structure analysis. Lorentz and polarization corrections were applied but no absorption correction $[\mu(\text{CuK}\alpha) = 2.75\ mm^{-1}]$ was made.

Solution and Refinement of the Structure

The structure was solved by application of the multi-solution weighted tangent formula [13] to reflections with E > 1.85. An E-map based on the solution with the highest absolute figure of merit (1.082) and the lowest residual index (24.21) revealed the positions of the Cu and Cl atoms.

The remaining non-hydrogen atoms of the organic molecules were located by successive difference-Fourier calculations. Anisotropic temperature factors were assigned to all non-hydrogen atoms. Neutral-atom complex scattering factors were used [14].

The refinement was made by minimization of $[\omega(k|F_o| - |F_c|)^2]$ k through iterative blocked full matrix least squares calculations including observed reflections with weights $\omega_i = [\sigma^2(F) + 5.95 \times 10^{-4} F^2]^{-1}$ (where $\sigma^2(F)$ is the variance based on counting statistics) with independent carbons in the rings until there was good convergence. At this point the carbon atoms were fixed in a rigid and regular hexagon, with C–C distances equal to 1.395(3)Å in order to calculate the hydrogen positions (C–H distance: 1.080(3) Å). The refinement was conducted until all atomic parameter shifts were smaller than their standard deviation. Table I gives final atomic parameters.

TABLE I. Fraction Atomic Coordinates (10^4) with their e.s.d.'s in Parentheses. The B_{eq} Values are the Equivalent Isotropic Temperature Factor [15].

Atom	x/a	x/b	x/c	B_{eq}
Cu	7500(0)	7500(0)	2500(0)	3.4(3)
Cl	1815(1)	1893(1)	6115(1)	5.87(4)
O	9468(1)	9914(1)	490(3)	5.5(1)
P	9131(1)	9424(1)	1462(1)	4.05(3)
C1A	9394(2)	9556(2)	3192(4)	4.7(1)
C2A	10151(1)	9478(1)	3400(3)	4.0(1)
C3A	10591(1)	10024(1)	3154(3)	5.0(1)
C4A	11293(1)	9945(1)	3346(3)	5.7(2)
C5A	11554(1)	9320(1)	3783(3)	6.0(2)
C6A	11114(1)	8774(1)	4029(3)	6.2(2)
C7A	10413(1)	8853(1)	3837(3)	5.2(1)
C1B	9299(2)	8541(2)	1063(4)	4.9(1)
C2B	9323(1)	8383(1)	−421(2)	4.0(1)
C3B	9946(1)	8382(1)	−1104(2)	4.7(1)
C4B	9967(1)	8238(1)	−2486(2)	5.6(2)
C5B	9365(1)	8096(1)	−3185(2)	5.5(2)
C6B	8742(1)	8098(1)	−2502(2)	5.7(2)
C7B	8720(1)	8241(1)	−1120(2)	5.0(1)
C1C	8229(2)	9592(2)	1365(5)	5.0(1)
C2C	8101(1)	10343(1)	1370(3)	4.8(1)
C3C	8012(1)	10702(1)	2576(3)	7.6(2)
C4C	7975(1)	11413(1)	2560(3)	11.1(4)
C5C	8028(1)	11765(1)	1337(3)	12.4(4)
C6C	8118(1)	11406(1)	132(3)	10.4(3)
C7C	8155(1)	10695(1)	148(3)	6.5(2)

Results and Discussion

The structure of $(2tbpo{\cdot}H^+)_2[CuCl_4]^=$ consists of discrete $[CuCl_4]^=$ anions and $[(C_{21}H_{21}PO)_2{\cdot}H^+]$ cations (Fig. 1).

Cu(II) ions are located at special position $\bar{4}$, coordinated to four chlorides in a tetrahedral geometry, according to symmetry conditions. The CuCl distance is 2.225(1)Å and the angles are: 105.2(5)° and 111.64(2)°, showing a slightly elongation with respect to T_d symmetry.

The organic part has a singular arrangement with pairs of tbpo molecules related by centers of inversion. This way, the structure seems to have unbalanced charges. However, since the synthesis occurs in an acidic environment, we may infer that H^+ species are at centers of inversion, building special kinds of short symmetrical hydrogen bonds between two tbpo molecules, with O–O distances equal to 2.324(6)Å.

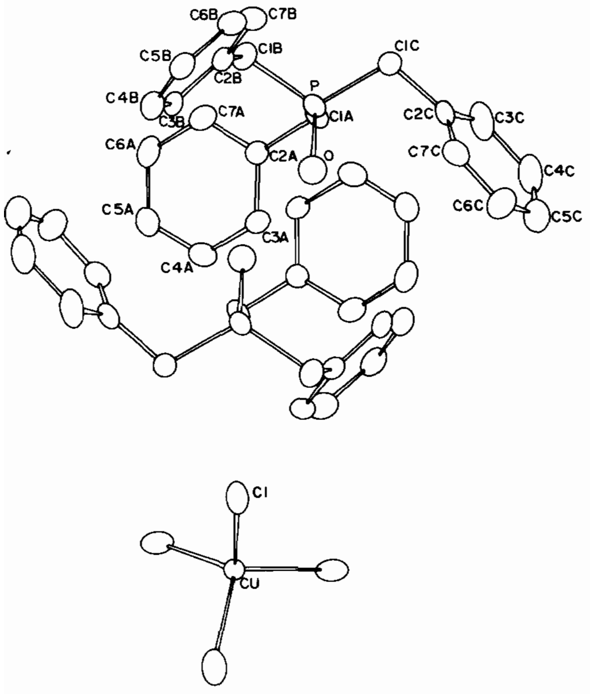

Fig. 1. Structure of $(2tbpo\cdot H^+)_2[CuCl_4]^=$.

This kind of hydrogen bond was previously proposed by Hadži [16] and confirmed by Harris *et al.* [11]. Distances and angles in tbpo molecules are as usual [17]. Phosphorus has tetrahedral hybridization showing high deformation in angles between oxygen and one of the carbons (Table II).

TABLE II. Principal Bond Distances (Å) and Angles (°) with their e.s.d.s in Parentheses.

O–P:	1.508(3)	O–P–C1B:	113.0(2)
P–C1A:	1804(4)	O–P–C1C:	106.2(2)
P–C1B:	1.806(4)	C1A–P–C1B:	107.0(2)
P–C1C:	1.800(4)	C1A–P–C1C:	107.7(2)
C1A–C2A:	1.505(4)	C1B–P–C1C:	110.0(2)
C1B–C2B:	1.499(5)	P–C1A–C2A:	113.4(3)
C1C–C2C:	1.490(5)	P–C1B–C2B:	114.6(3)
O–P–C1A:	112.8(2)	P–C1C–C2C:	110.2(3)

The electronic spectra of the $[CuCl_4]^=$ anion showed the d–d transitions in the near infrared region at 1050 nm (9520 cm^{-1}) and 1600 nm (6250 cm^{-1}) (Fig. 2). The band that appears at 415 nm (24100 cm^{-1}) is a charge transfer band. In nitromethane or 1,2-dichlorethane solutions changes in color of the complex occur and the spectrum in the visible region is completely different: two bands at 465 nm ($\epsilon \cong 1830$) and 375 nm ($\epsilon \cong 710$) were observed.

The compound with the $[CuBr_4]^=$ anion showed two bands corresponding to d–d transitions at 1100 nm (9090 cm^{-1}) and 1600 nm (6250 cm^{-1}) (Fig. 3).

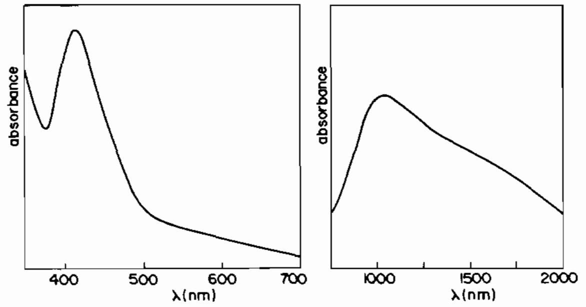

Fig. 2. Electronic spectra of the complex $(2tbpo\cdot H^+)^2[CuCl_4]^=$.

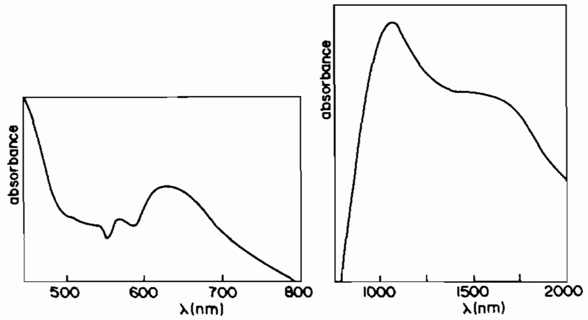

Fig. 3. Electronic spectra of the complex $(2tbpo\cdot H^+)_2[CuBr_4]^=$.

In the visible region between 800 and 400 nm several bands occurred at 630 nm (15870 cm^{-1}), 570 nm (17540 cm^{-1}), 540 nm (18520 cm^{-1}) and 510 nm (19600 cm^{-1}). They are probably charge transfer bands [6]. On the other hand the transition at 15870 cm^{-1} could also be a d–d transition band [18].

The compounds $(LH)_2CuCl_4$ and $(LH_2)CuCl_4$ (LH = N-methylpiperidinium and LH_2 = N,N′-dimethylpiperazinium cations) have the $[CuCl_4]^=$ anion with a distorted tetrahedral structure [6]. They show d–d transition bands at 6170 and 9090 cm^{-1}, 6330 and 9430 cm^{-1}, respectively. The charge transfer bands appear at 24390, 33900 and 42550 cm^{-1}, 24390, 33670 and 41670 cm^{-1}, respectively. We could not observe the last two bands (near 33500 and 42000 cm^{-1}) because tbpo absorbs strongly in this region.

Simonsen and co-workers [19] proposed a correlation between the frequency of the d–d transition above 9000 cm^{-1} and the dihedral angle θ, as a measurement of the distortion of the tetrahedral from T_d to D_{2d} symmetry. Cs_2CuCl_4 has the anion with $\theta = 129.2°$ (the nearest known with T_d symmetry) and a d–d band at 9050 cm^{-1}; $[(C_6H_5)CH_2CH_2NH_2CH_3]_2CuCl_4$ has the $[CuCl_4]^=$ anion with a D_{2d} symmetry ($\theta = 180°$) and a d–d band at 16100 cm^{-1}.

The compound $(2tbpo\cdot H^+)_2[CuCl_4]^=$ has an anion distorted very little from tetrahedral symmetry (Cl–Cu–Cl angles are 105.2 and 111.6°). Thus we did not find the correlation proposed by those authors; the N-phenylpiperazinium halocuprates do not show this correlation either [5].

The ESR powder spectra of the $[CuCl_4]^=$ complex is shown in Fig. 4 and it is in agreement with a T_d symmetry with a slight rombic distortion ($g_1 \neq g_2 \neq g_3$, but the g_1 value is near the g_2 value). The g_3 value (z direction of the complex) shows that the fundamental one electron state is d_{z^2} symmetry [20].

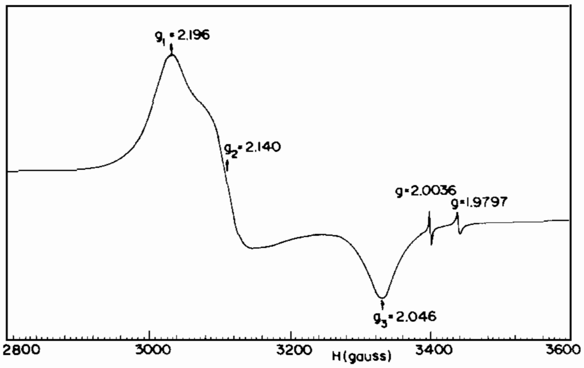

Fig. 4. Electron Spin Resonance spectra of the complex $(2tbpo{\cdot}H^+)_2[CuCl_4]^=$ in X-band and room temperature (powder sample).

The broad electronic band, with a maximum near 6250 cm^{-1}, is in agreement with the small rombic distortion showed by the ESR spectra, where a slight splitting of the d_{xz} and d_{yz} states is observed. The small crystals of the complex $(2tbpo{\cdot}H^+)_2[CuCl_4]^=$ did not permit us to obtain the polarised electronic absorption spectra to clarify this point.

The IR spectra of both complexes are very similar to each other (Fig. 5). These spectra can be compared to those of the adducts $2(tbpo){\cdot}HClO_4$ and $2(tbpo){\cdot}HI$ (Fig. 6). The spectra of all the compounds exhibited bands in the region 1600–800 cm^{-1}, and an especially broad band centered at 1430 cm^{-1}. As no $\nu(O\cdots H)$ band is observed in the region 3000–2000 cm^{-1}, that band is assigned to a strong hydrogen bond corresponding to the cation [tbpo $\cdots H^+ \cdots$ tbpo] [11, 21] and therefore corroborates the results of the X-ray diffraction study.

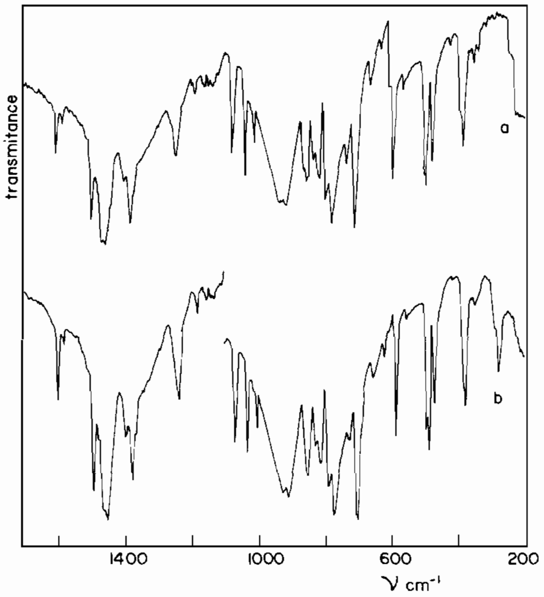

Fig. 5. IR spectra in the region 1600–200 cm^{-1} of the complexes: a) $(2tbpo{\cdot}H^+)_2[CuCl_4]^=$; b) $(2tbpo{\cdot}H^+)_2[CuBr_4]^=$, (CsI disks).

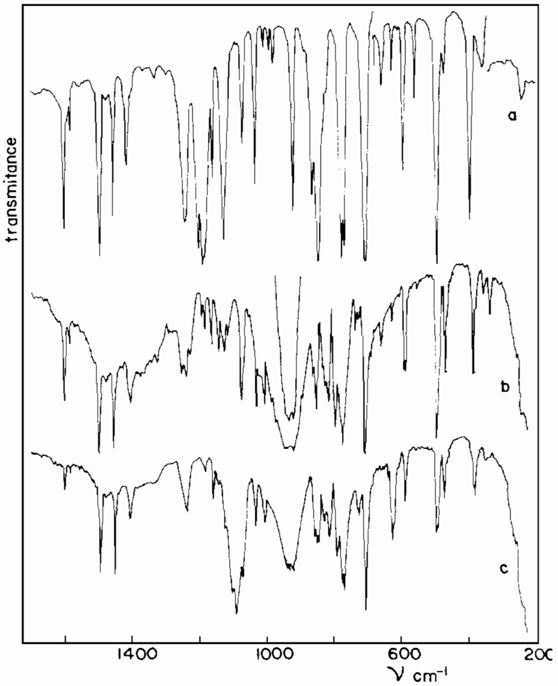

Fig. 6. IR spectra in the region 1600–200 cm^{-1} of the compounds: a) tbpo; b) $2(tbpo){\cdot}HI$; c) $2(tbpo){\cdot}HClO_4$.

References

1 N. M. Karayannis, C. M. Mikulski and L. L. Pytlewski, *Inorg. Chim. Acta, 5,* 69 (1971).

2 J. A. Bertrand and A. R. Kalyanaraman, *Inorg. Chim. Acta, 5,* 342 (1970).

3 J. A. Bertrand, S. L. Grahan, H. M. Deutsch and D. G. Van Derveer, *Inorg. Chim. Acta, 19,* 189 (1976).

4 D. W. Smith, *Coord. Chem. Rev., 21,* 93 (1976) and references cited therein.

5 L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chem., 18,* 184 (1979).

6 G. Marcotrigiano, L. Menabue, G. C. Pellacani and M. Saladini, *Inorg. Chim. Acta, 34,* 43 (1979).

7 R. D. Willett, O. L. Liles, Jr. and C. Michelson, *Inorg. Chem., 6,* 1885 (1967).

8 R. L. Harlow, W. J. Wells, G. W. Watt and S. H. Simonsen,

Inorg. Chem., 13, 2106 (1974).
9 L. Antolini, L. Menabue, G. C. Pellacani, M. Saladini, G. Marcotrigiano and W. Porzio, *J. Chem. Soc. Dalton,* 1753 (1981).
10 L. Antolini, L. Menabue, M. Saladini and P. Morini, *Inorg. Nucl. Chem. Letters, 17,* 41 (1981).
11 G. S. Harris, F. Inglis, J. McKechnie and K. K. Cheung, *Chem. Commun.,* 442 (1967).
12 F. G. Mann, I. T. Miller and F. H. C. Stewart, *J. Chem. Soc.,* 2832 (1954).
13 G. Germain, P. Main and M. M. Woolfson, *Acta Cryst., A27,* 368 (1971).
14 International Table for X-ray Crystallography, Vol. IV, Birmingham, K. Press (1974).
15 W. C. Hamilton, *Acta Cryst., 12,* 609 (1959).
16 D. Hadži, *J. Chem. Soc.,* 5128 (1962).
17 G. Bandoli, G. Bortolozzo, D. A. Clemente, U. Croatto and C. Panattoni, *J. Chem. Soc(A),* 2778 (1970).
18 P. S. Braterman, *Inorg. Chem., 2,* 448 (1963).
19 R. L. Harlow, W. J. Wells, G. W. Watt and S. H. Simonsen, *Inorg. Chem., 14,* 1768 (1975).
20 B. J. Hathaway, *Coord. Chem. Rev., 35,* 211 (1981).
21 A. Derbli Pinto and A. C. Massabni, *Ecl. Quím., 5,* 17 (1980).