Fume hood), and the dark-blue solution so formed is added to a slurry of 4.01 g (0.0091 mole) of Hp-H_2 in 30 mL of hot dimethylformamide. The grey-green mixture is refluxed gently, with stirring, for 4 hours and allowed to cool. After filtration the solid residue is washed thoroughly with cold dimethylformamide and then with cold methanol. The olive-green powder is dried by suction and stored *in vacuo* over silica gel. Yield of the dihydrate is 2.53 g (0.0047 mole, 51%). *Anal.* Calcd. for $C_{26}H_{18}N_8O_3V$: C, 57.69; H, 3.35; N, 20.70. Found: C, 57.76; H, 2.95; N, 21.06.

Properties

The very insoluble, oxygen- and moisture-insensitive complex obeys the Curie law, after allowance is made for TIP corrections,[12] with an effective magnetic moment of 1.87 BM at 300°K.

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9. TEMPLATE SYNTHESES OF COMPLEXES WITH PARTIALLY UNSATURATED MACROCYCLIC LIGANDS

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Checked by MICHAEL GERY† and BRADFORD B. WAYLAND†

There are macrocyclic ligands of biochemical interest that contain a modified porphine skeleton in varying degrees of reduction compared to the porphine nucleus; one such species is tetrahydrocorrin.[1,2] The reaction between (1,2-

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alkanediamine)(1,2-arylenediamine)metal(II) diacetates or dichlorides and 2-malonaldehydes with electron-withdrawing substituents has been successful only when the complexes of copper(II) diacetate[3] are used.

A. BROMOMALONALDEHYDE (Bromopropanedial)

$$Br_2 + (C_2H_5O)_2CHCH_2CH(C_2H_5O)_2 + 2H_2O \xrightarrow{\text{acid}}$$
$$OHCCHBrCHO + 4C_2H_5OH + HBr$$

Procedure

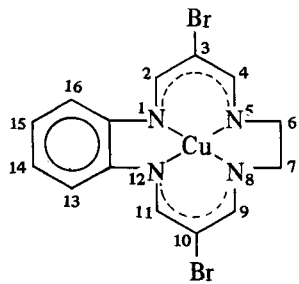
Concentrated hydrochloric acid (20 mL) is added to a vigorously stirred solution of 100 mL (0.34 mole) of 1,1,3,3-tetraethoxypropane [malonaldehyde bis-(diethyl acetal)] in 100 mL of distilled water. To this is added, dropwise, 17.5 mL (0.34 mole) of bromine. (■ **Caution.** *Use a fume hood.*) The coloration of the bromine disappears immediately if the dropping rate is sufficiently slow. No increase in temperature is observed.

The reaction mixture is taken to a slush in a rotary evaporator (55°/25 torr) and filtered through a sintered-glass filter. The pale-yellow, crystalline product is dried by suction and stored *in vacuo* over silica gel. Yield 29.35 g (0.19 mole, 57%) *Anal.* Calcd. for $C_3H_3O_2Br$: C, 23.87; H, 2.00; Br, 52.93. Found: C, 23.95; H, 1.88; Br, 53.2.

B. [3,10-DIBROMO-1,6,7,12-TETRAHYDRO-1,5,8,12-BENZOTETRAAZACYCLOTETRADECINATO(2−)]COPPER(II) (Cu(II)[6,13-Br_2-2,3-Bzo[14]-2,4,6,11,13-pentaenato(2−)-1,4,8,11-N_4])

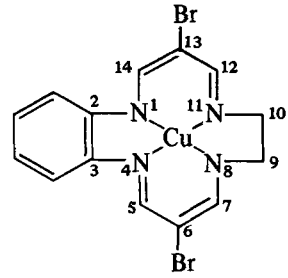
$$[(CH_3COO)_2Cu(en)C_6H_4(NH_2)_2] + 2BrCH(CHO)_2 \longrightarrow$$

$$2CH_3COOH + 4H_2O +$$



en = $H_2NC_2H_4NH_2$

Numbering for abbreviation



Procedure

A solution of 1.08 g (0.01 mole) of *o*-phenylenediamine (1,2-benzenediamine) in 100 mL of dry ethanol is added very slowly with vigorous stirring to a solution of 2.0 g (0.01 mole) of reagent grade copper(II) acetate. The dark-green precipitate is filtered through a sintered-glass filter *without* suction, washed with dry ethanol *without* suction, and then washed into a 250-mL conical flask with approximately 100 mL of dry ethanol from a wash bottle. To this suspension of the monoamine complex, a solution of 0.65 mL (0.01 mole) of ethylenediamine (1,2-ethanediamine) in 50 mL of dry ethanol is added dropwise over an extended period at 10°. The mixture is allowed to remain in the dark for 24 hours at this temperature, with constant vigorous stirring.

The reaction mixture is taken to 2° and a solution of 3.08 g (0.02 mole) of bromomalonaldehyde in 50 mL of dry ethanol is added. This green reaction mixture is stirred vigorously in the dark for 7 days at 2° until the suspended solid is black. This solid is filtered, washed thoroughly with dry ethanol, and dried *in vacuo* over silica gel. The yield of anhydrous product is 2.13 g (0.0046 mole, 46%). *Anal.* Calcd. for $C_{14}H_{12}N_4CuBr_2$: C, 36.59; H, 2.63; N, 12.19. Found: C, 36.60; H, 2.53; N, 12.57.

Properties

The very insoluble black solid affords the required peaks in the mass spectrum for $C_{14}H_{12}N_4CuBr_2$ at 280° with a beam strength of 19 eV. The base peak is given by $H^{79}Br$.

General Remarks

The low reaction temperature is used to prevent the reaction between free *o*-phenylenediamine and the dialdehyde, which gives the macrocycle (7,16-dibromo-5,14-dihydrodibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine) even in the absence of metal ions.[4] The above reaction scheme is also successful when $NO_2CH(CHO)_2$ or $C_2H_5OOCCH(CHO)_2$ is used.

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