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Polymeric Ligands. 9. Oxidation–Reduction Properties of Some Polymeric Thiosemicarbazides Containing Copper Ions[1]

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ABSTRACT: The syntheses of three new poly(thiosemicarbazides) are reported along with those of the respective copper(I) and copper(II) complexes. Oxidation–reduction reactions of the copper complexes of five polymeric thiosemicarbazides, wherein the Cu(I)–Cu(II) "redox" system was employed to reduce or oxidize various organic substrates, are described. "Redox" properties appeared to be related to the nature of the polymer employed to hold the copper.

Results and Discussion

In 1962, Campbell, Foldi, and Tomic[3] reported the preparation of two poly(thiosemicarbazides) (I, II; see Scheme I) which were highly selective for the preferential complexation of copper(II). A problem in utilizing these materials as ion exchangers was that the only useful elutant was aqueous sodium cyanide which, of course, presented certain handling hazards. In attempting to devise selective ion exchange systems which might lower copper(II) concentrations in brass mill effluents to acceptable proportions, we wished to be able to elute the complexed copper(II) from I and II with dilute mineral acid, if possible. Thus, in preparing III–V we attempted to introduce varying degrees of steric hindrance which might weaken the bonding of copper(II) to the poly(thiosemicarbazides). Structures for the copper(II) complexes of I and II are reported[3] and when models of the copper(II) complexes of III–V were constructed, it appeared that the desired steric interactions had been introduced. These interactions were insufficient to allow significant elution with dilute mineral acids, although some improvement was achieved. We then turned to a search for other elutants. Among the large number tried were warm aqueous solutions of 1,4-benzoquinone and hydroquinone. These proved to be successful elutants for the copper(II) complexes of I–V. However, knowing that hydroquinone can be oxidized somewhat easily, we were concerned lest oxidation to 1,4-benzoquinone might have occurred in which case the complexed copper(II) ion would have been reduced to copper(I) thus changing the identity of the ions collected by exchange. However, we could detect no 1,4-benzoquinone.

Having thought about the possibility of oxidation–reduction reactions occurring, we decided to actually attempt a number of these using IIa. We found that upon contacting benzaldehyde with IIa, very good yields of benzoic acid were obtained (see Table I) and that IIa was converted to IIb. There was no difference between IIb prepared from IIa and IIb prepared directly from II and cuprous salts. IIb could be readily oxidized back to IIa with a number of reagents (see Table II), and again there was no difference in the IIa species regardless of how it was prepared. Thus, copper could be repeatedly oxidized or reduced with various substrates without coming off the ion exchanger except when 1,4-benzoquinone was reduced to hydroquinone using IIb.

In the oxidation of benzaldehyde to benzoic acid, the rate of conversion of aldehyde to acid in a 24-h period increased from 18 to 100% as the mole ratio of aldehyde to copper(II) went from 1:1 to 1:5. Further, we found that the nature of the poly(thiosemicarbazide) used to form Ia–Va profoundly altered the yields of benzoic acid over the same reaction time under identical reaction conditions (see Table III).

It is interesting to note that a special situation exists here in that the copper is so tightly bound to the poly(thiosemicarbazide) that it is possible to carry out oxidation–reduction reactions under extremely simple reaction conditions which give good yields of various products and no loss of copper (save in the quinone–hy-

Table I
Reaction of IIa with Various Organic Compounds

organic reactant, × 10^{-3} mol	copper content × 10^{-3} mol^a	temp, °C	method^b	product	% yield 24 h	% yield 48 h
propionaldehyde, 0.1	0.58	40–50	S	propionic acid	60	82
benzaldehyde, 0.1	0.58	70–80	S	benzoic acid	84	83
benzaldehyde, 0.1	5.26	70–80	C	benzoic acid	100^c	
benzyl alcohol, 0.1	0.58	70–80	S	benzoic acid	30	67
cyclohexanol, 1.0	5.26	80–90	C	cyclohexanone	100^c	

^{a} No detectable copper losses occurred in any of the reactions within the limits of experimental error. ^{b} S = slurry; C = column, 1 cm diameter × 3 cm length. ^{c} Flow rate of 20 mL/h.

Table II
Reaction of IIb with Various Compounds

organic reactant, × 10^{-3} mol	copper content^a × 10^{-3} mol	temp, °C	time, h	method^b	result
nitrosobenzene, 1.0	4.2	70–80	24	S	azoxybenzene (10% yield)
nitrocyclohexane, 6.0	21.5	70–80	24	S	cyclohexanone oxime (10% yield)
1,4-benzoquinone, 4.0	14.2	80–90	12	S	hydroquinone (100% yield)
$KMnO_4$^{c}	2–22	25	immediate	S, C	MnO_2 (100% yield)

^{a} Copper loss occurred only with the reaction forming hydroquinone. Other copper concentrations were constant within the limits of experimental error. ^{b} S = slurry; C = column. ^{c} 0.1 M solution.

Scheme I
Preparation of Poly(thiosemicarbazides)

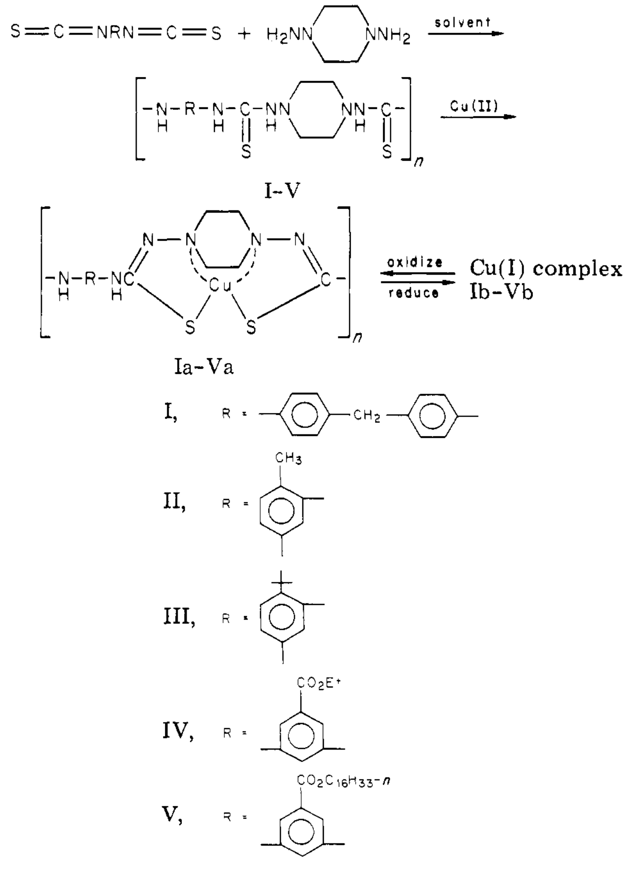

Table III
Comparison of Yields Obtained by Utilization of Ia–Va for Oxidation of Benzaldehyde to Benzoic Acid^{a,b}

complex	% yield after 24 h
Ia	41
IIa	84
IIIa	35
IVa	16
Va	17

^{a} Benzaldehyde (0.01 M, 10 mL) was used as a reactant. Each complex contained the same amount of copper. The mole ratio of copper–benzaldehyde was 6:1 and the reactions were carried out at 70–80 °C. ^{b} Slurry reactions.

droquinone reaction). The group transferring electrons is a metal ion complexed so strongly that it cannot be removed by most potential elutants. The only effective elutants known in this polymer system are cyanide ion, 1,4-benzoquinone, and hydroquinone. Even ethylenediaminetetraacetic acid is not an effective elutant.[3] Thus, while the same reactions might be carried out with simple ion exchange resins, losses of metal ion would be high because it is so easy to elute metal ions from such resins with both simple inorganic ions and the organic reactants and products which might act as ligands for the "redox" couple. There seems to be no significant loss or deterioration of polymer in these reactions either. Further, it may be possible to control reaction rates by altering the polymer structure holding the metal ion (see Table III).

Further studies of this interesting unusual "redox" polymer are underway, and a search for polymers which will bind other variable valent metal ions as tightly is in progress.

Experimental Section

General. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxvill, Tenn. Infrared spectra were taken on a Perkin-Elmer 137 infrared spectrophotometer in potassium bromide wafers. Copper analyses were done on a Perkin-Elmer 290B atomic absorption spectrophotometer. Polymeric complexes were analyzed by destroying the organic matter via nitric acid oxidation and analyzing the resultant solution by atomic absorption spectrometry. I and II were prepared by the directions of Campbell, Foldi, and Tomic.[3] Thiophosgene was obtained from Aldrich Chemicals, Inc. *tert*-Butyl-2,4-diaminobenzene was synthesized by reduction of *tert*-butyl-2,4-dinitrobenzene.[1,4,5] Ethyl 3,5-diaminobenzoate was prepared by reduction[1,5] of ethyl 3,5-dinitrobenzoate which was in turn prepared by reaction of 3,5-dinitrobenzoyl chloride with ethanol.[6] *n*-Hexadecyl 3,5-dinitrobenzoate and *n*-hexadecyl 3,5-diaminobenzoate were prepared in the same way as the ethyl homologue using *n*-hexadecyl alcohol in place of ethanol.[6]

Preparation of *tert*-Butyl-2,4-(diisothiocyanato)benzene. Thiophosgene, 25 g (0.217 mol), was added to 150 mL of water. The mixture was maintained at 0–5 °C and stirred vigorously. A mixture of 13.9 g (0.085 mol) of *tert*-butyl-2,4-diaminobenzene in 100 mL of chloroform was slowly added to the flask. The mixture was stirred at 0–5 °C for an additional 2 h. It was then allowed to warm to room temperature and was stirred for 24 h. After this time, the organic layer was separated and evaporated to dryness under a stream of nitrogen. The product was recrystallized from ethanol–water (51%; mp 37–8 °C). Anal. Calcd for $C_{12}H_{12}N_2S_2$: C, 58.06; H, 4.84; N, 11.29; S, 25.81. Found: C, 58.06; H, 4.80; N, 11.34; S, 26.00. Infrared: 755 (s), 825 (s), 865 (s), 920 (m), 1010 (m), 1080 (m), 1130 (w), 1185 (w), 1265 (w), 1350 (m), 1390 (w), 1475 (s), 1540 (s), 1580 (s), 2025 (s), 2850 (m) cm^{-1} (w = weak absorption; m = medium absorption; s = strong absorption).

Preparation of III. 1,4-Diaminopiperazine, 4.4 g (0.026 mol), was added to 100 mL of dimethyl sulfoxide (Me_2SO) at 50 °C. To this mixture was added 7.17 g (0.026 mol) of *tert*-butyl-2,4-(diisothiocyanato)benzene. The mixture was vigorously stirred for 4.5 h at 50 °C and for an additional 48 h at room temperature. The polymer was isolated by precipitation in water (yield 88%). The polymer had an intrinsic viscosity of 0.27 and was soluble in Me_2SO and dimethylformamide. The polymer softened at 225–230 °C. Anal. Calcd for $C_{16}H_{24}N_6S_2$: C, 52.75; H, 6.59; N, 21.95; S, 17.60. Found: C, 52.55; H, 6.74; N, 21.95; S, 17.53. Infrared: 750 (s), 820 (m), 1000 (s), 1110 (s), 1250 (m), 1350 (m), 2100 (m), 2900 (s), 3175 (s) cm^{-1}.

Preparation of Ethyl 3,5-(Diisothiocyanato)benzoate. Thiophosgene, 6.34 g (0.055 mol), was added to 100 mL of vigorously stirred water at 0–5 °C. Ethyl 3,5-diaminobenzoate, 4.5 g (0.025 mol), in 50 mL of chloroform was slowly dropped into the flask. After all the diamine had been added, the mixture was stirred for an additional 2 h at 0–5 °C. The mixture was then allowed to warm to room temperature and stirred for an additional 24 h. The organic layer was separated and evaporated to dryness under a stream of nitrogen. The crude material was dissolved in petroleum ether (bp 40–60 °C) and decolorized using activated charcoal. The material was recrystallized three times from petroleum ether. The crystals obtained (60%) had a melting point of 78–80 °C. Anal. Calcd for $C_{11}H_8N_2O_2S_2$: C, 50.00; H, 3.05; N, 10.60; S, 24.24. Found: C, 49.93; H, 3.05; N, 10.55; S, 24.41. Infrared: 728 (s), 735 (s), 785 (m), 838 (m), 865 (m), 925 (m), 1020 (m), 1080 (m), 1160 (m), 1180 (m), 1275 (s), 1340 (s), 1460 (m), 1540 (s), 1630 (m), 1725 (s), 3100 (m) cm^{-1}.

Preparation of IV. 1,4-Diaminopiperazine, 1.276 g (0.00838 mol), was added to 500 mL of Me_2SO at 60 °C. To this mixture was added 2.213 g (0.00838 mol) of ethyl 3,5-(diisothiocyanato)benzoate. The mixture was vigorously stirred for 3.5 h at 60 °C. The mixture was then brought to room temperature and stirred for an additional 24 h. The polymer was obtained by precipitation in water. The polymer had an intrinsic viscosity of 0.28 and was soluble only in Me_2SO. Yields were quantitative. The polymer softened at 230–235 °C. Anal. Calcd for $C_{15}H_{20}N_6O_2S_2$: C, 47.40; H, 5.26; N, 22.10; S, 16.85. Found: C, 47.04; H, 5.56; N, 21.85; S, 16.81. Infrared: 710 (m), 780 (m), 870 (m), 1010 (m), 1030 (m), 1115 (m), 1250 (s), 1325 (m), 1375 (m), 1470 (m), 1520 (s), 1620 (s), 1725 (s), 3000 (m), 3250 (m) cm^{-1}.

Preparation of *n*-Hexadecyl 3,5-(Diisothiocyanato)benzoate. Thiophosgene, 5 g (0.0435 mol), was added to 100 mL of vigorously stirred water maintained at 0–5 °C. A mixture of 6.65 g (0.0172 mol) of *n*-hexadecyl 3,5-diaminobenzoate in 100 mL of chloroform was dropped into the flask. The mixture was stirred at 0–5 °C for an additional 2 h and stirred at room temperature for an additional 24 h. The organic layer was separated and evaporated to dryness under a stream of nitrogen. The crude material was dissolved in petroleum ether (bp 40–60 °C) and decolorized using activated charcoal. This solution was chilled and a white solid was obtained. This material was recrystallized three times using petroleum ether. The white powder obtained (40%) had a melting point of 62–64 °C. Anal. Calcd for $C_{25}H_{36}N_2O_2S_2$: C, 65.22; H, 7.83; N, 6.09; S, 13.91. Found: C, 65.20; H, 7.73; N, 6.09; S 13.92. Infrared: 725 (s), 730 (s), 740 (s), 880 (s), 875 (w), 920 (w), 945 (s), 1000 (w), 1010 (w), 1040 (m), 1235 (s), 1330 (s), 1390 (w), 1430 (m), 1460 (s), 1580 (s), 1720 (s), 2100 (s), 2850 (s) cm^{-1}.

Preparation of V. 1,4-Diaminopiperazine, 0.656 g (0.0043 mol), was added to 150 mL of dry pyridine at 50 °C. To this mixture was added 1.98 g (0.0043 mol) of *n*-hexadecyl 3,5-(diisothiocyanato)benzoate. The mixture was vigorously stirred for 2 h at 50 °C and for an additional 24 h at room temperature. The polymer was isolated by precipitation in water. The polymer had an intrinsic viscosity of 0.55. The polymer was soluble in pyridine and aniline. It was not soluble in Me_2SO. The polymer had a softening temperature of 240–246 °C. The yield was 83%. Anal. Calcd for $C_{29}H_{48}N_6O_2S_2$: C, 60.44; H, 8.33; N, 14.55; S, 11.10. Found: 60.15; H, 7.99; N, 14.55; S, 10.46. IR: 710 (m), 780 (m), 880 (m), 1010 (m), 1125 (s), 1250 (s), 1335 (m), 1470 (m), 1520 (s), 1610 (s), 1740 (s), 2800 (s), 3000 (s), 3350 (s) cm^{-1}.

Table IV
Copper Analyses for Ia–Va

polymer	calcd, %	found, %
Ia	13.82	13.80
IIa	16.57	16.85
IIIa	14.39	14.64
IVa	14.93	15.21
Va	9.96	10.10

Preparation of Ia–Va. A dimethyl sulfoxide solution of copper(II) acetate was added to a solution of a polymer in a proper solvent (Me_2SO or pyridine) or the polymers were stirred with copper(II) acetate aqueous solutions (50 ppm) containing a few drops of glacial acetic acid. Theoretical loading of the polymers with copper(II) was achieved in either case within values of ±0.30% (see Table IV). The copper(II) complexes were insoluble in water, Me_2SO, or pyridine.

Oxidation of Benzaldehyde with IIa in a Slurry. IIa, 200 mg (16.5% of copper(II), 0.58×10^{-3} mol), was placed in a flask with 10 mL of 0.01 M benzaldehyde in 95% ethanol and 20 mL of water. The mixture was stirred at 70–80 °C for 24 h. The reaction mixture was cooled to room temperature and the IIb removed by filtration. The filtrate was titrated with 0.01 M sodium hydroxide. Benzoic acid was found in 84% yield. The product also was isolated and identified by comparison with the infrared spectrum of authentic benzoic acid. Other slurry oxidations were carried out in the same manner (see Tables I–III).

Oxidation of Benzaldehyde with IIa in a Column. A jacketed column using a IIa bed of 3 cm in length and 1 cm in diameter (1.8 g of IIa; 16.5% Cu) was prepared and warmed with steam to 70–80 °C. A mixture of 10 mL of 0.01 M benzaldehyde in 95% ethanol and 20 mL of water was passed through the column at a flow rate of 20 mL/h. The yield of benzoic acid was quantitative.

All column oxidations were carried out in the same manner (see Tables I and II). Cyclohexanone was isolated as the 2,4-dinitrophenylhydrazone.[6]

Preparation of Ib–Vb. Copper(I) chloride was dissolved in concentrated hydrochloric acid and a large amount of water added to precipitate pure copper(I) chloride. The precipitated salt was washed with water and added to sodium hydroxide solution to form hydrated copper(I) oxide which was separated and added to acetic acid. The mixture was stirred for 2–3 h until a blue solution formed. The solution was filtered and the polymer (I–V) dispersed in the filtrate and stirred for 3–4 days. The insoluble filtered products were light brown in color and were washed with acetic acid and water. When water slurries of this polymer were treated with standard potassium permanganate solutions, the polymers Ib–Vb were converted quantitatively to Ia–Va. No damage to the polymer occurred as long as no excess potassium permanganate was present.

Reduction of Nitrocyclohexane with IIb. IIb, 10 g (13.8% of copper, 21.5×10^{-3} mol of copper(I)), was slurried with 40 mL of 0.4 N alcoholic potassium hydroxide and 780 mg of nitrocyclohexane (6×10^{-3} mol) was added to the flask. The mixture was refluxed and stirred for 36 h. IIa was separated by filtration and the filtrate was evaporated to dryness. The residue was neutralized with dilute hydrochloric acid and extracted with ether. The ether layer was dried (Na_2SO_4). Evaporation of the ether yielded 80 mg of white crystals (10%). The infrared spectrum of the crystals was identical with that of authentic sample of cyclohexane oxime.

Reduction of Nitrosobenzene with IIb. A mixture consisting of 110 mg (1×10^{-3} mol) of nitrosobenzene, 3 g (9.1% copper, 4.2×10^{-3} mol of copper(I)) of IIb, and 25 mL of ethanol was refluxed under stirring for 24 h. After filtration of IIa, the filtrate was decolorized with charcoal and evaporated to dryness to yield brown crystals (10%). The product had infrared and ultraviolet spectra identical with that of an authentic sample of azoxybenzene.

Reduction of 1,4-Benzoquinone with IIb. IIb, 10 g (9.1% of copper(I) 14.2×10^{-3} mol of copper), was added to a solution containing 432 mg (4×10^{-3} mol) of 1,4-benzoquinone and 50 mL of 10% hydrochloric acid solution. The mixture was refluxed and stirred for 12 h. The IIa was removed by filtration and the filtrate was neutralized with dilute sodium hydroxide solution and extracted with ether. The ether layer was separated, dried (Na_2SO_4), treated with activated charcoal, and evaporated to dryness. The residue was 135 mg (31%) of white crystals, whose infrared spectrum was identical with that of an authentic hydroquinone sample. The copper content of the polymer after the reaction was 6.8%. Titration of reaction mixtures with cerium(IV) immediately subsequent to removal of IIa showed that yields were quantitative.

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Linear Oligopeptides. 59.[1] Stereochemical Analysis of *N-tert*-Butyloxycarbonyl-L-prolylsarcosine and *N-tert*-Butyloxycarbonylsarcosylsarcosine in the Solid State and in Solution

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ABSTRACT: An analysis of the conformational properties of *N-tert*-butyloxycarbonyl-L-prolylsarcosine and *N-tert*-butyloxycarbonylsarcosylsarcosine was carried out in the solid state and in solution. The stereochemical preferences of the two N-protected dipeptides were found to be close under the experimental conditions examined. In the solid state a cis tertiary urethane bond and an intermolecular O–H···O=C (amide) hydrogen bond characterize the molecular and crystal structures. Even in a solvent of low polarity at high dilution the amounts of intramolecularly hydrogen-bonded forms, if any, appear to be negligible.

As a part of our continuing study[1,3–8] of the occurrence, both in the solid state and in solution, of the oxy analogues of the 3 → 1 and 4 → 1 intramolecularly hydrogen-bonded peptide conformations (also called oxy-C_7 and oxy-C_{10} forms, respectively), the present report provides information from infrared absorption (IR) and X-ray diffraction analysis of the conformational preferences of two *N-tert*-butyloxycarbonyl (*t*-Boc) dipeptides containing exclusively *N*-alkyl-α-amino acid residues, namely *t*-Boc-L-Pro-Sar-OH and *t*-Boc-Sar-Sar-OH.

On the basis of an IR absorption investigation in the solid state, Deber[9] has recently proposed for *t*-Boc-L-Pro-Sar-OH the possible formation of an antiparallel dimer, where the –OH proton of the –COOH group of each molecule is hydrogen bonded to the peptide C=O group of its neighbor, forming a 14-membered ring structure between two molecules, closed with two hydrogen bonds.

The only N-protected dipeptide of the aforementioned type (i.e., lacking amide protons) so far examined by X-ray diffraction is Z-L-Pro-Pro-OH[10] (Z stands for benzyloxycarbonyl–). The peptide backbone exhibits a sharp bend at the site of the cis bond between the N-blocking group and the first prolyl residue. Also, a network of intermolecular hydrogen bonds of the type O–H···O=C (urethane type) is formed in the crystal. In contrast, the free H_2^+-Sar-Sar-O^- peptide has the tertiary peptide bond in the cis configuration according to the X-ray diffraction study of this molecule carried out by Stezowski and Hughes.[11]

Experimental Section

Materials. The details of the synthesis of *t*-Boc-L-Pro-OH,[4] *t*-Boc-Sar-OH,[12] *t*-Boc-L-Pro-OMe (OMe stands for methoxy),[4] *t*-Boc-L-Pro-Sar-OMe,[5] *t*-Boc-L-Pro-Sar-OH,[5] *t*-Boc-Sar-OMe,[12] *t*-Boc-Sar-Sar-OMe,[12] and *t*-Boc-Sar-Sar-OH[12] have already been reported.

Ac-Sar-OH (where Ac is acetyl)[13] was prepared by reacting acetic anhydride with sarcosine at pH 8.5; the reaction mixture was brought to pH 3 with dilute HCl and evaporated to dryness under reduced pressure. The resulting product was dissolved in chloroform, dried over anhydrous sodium sulfate, filtered, and evaporated to small volume under reduced pressure, mp 134 °C.

Infrared Absorption. Infrared absorption spectra were recorded using a Perkin-Elmer Model 580 spectrophotometer. For the solution measurements a 10-cm cell was employed at low concentrations ($\sim 10^{-4}$ M), whereas cells with path lengths of 0.2, 0.1, and 0.05 mm were used for measurements at high concentrations ($\sim 10^{-2}$ M).

Trimethyl phosphate (TMP), deuteriochloroform (99.8% *d*), and deuterium oxide (99.9% *d*) were purchased from Merck, Darmstadt. For the solid measurements the KBr disk technique was employed. The band positions are accurate to ± 1 cm^{-1}.

X-ray Diffraction. Crystals of *t*-Boc-L-Pro-Sar-OH and *t*-Boc-Sar-Sar-OH, both in the form of colorless needles, were grown from different organic solutions (acetone and ethyl acetate usually give better quality crystals).

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