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A Novel, Nonelectrochemical Synthesis of the Organic Superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

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Bis(ethylendithio)tetrathiafulvalene (BEDT-TTF or ET) can be oxidized with Cu(SCN)$_2$ to yield superconducting, microcrystalline κ-(ET)$_2$Cu(NCS)$_2$. The reaction is achieved either by heating a suspension of the reactants in various organic solvents or by ultrasound agitation at room temperature. The formation of the title compound was established by X-ray diffractograms, FT-IR and ESR spectroscopy. Susceptibility measurements revealed superconducting transition temperatures of 9.5—10 K. The clearly observed Meissner effect suggests superconductivity to be a bulk property of the so-obtained powder samples.

The development of organic superconductors based on tetrachalcogenafulvalenes, especially bis(ethylendithio)tetrathiafulvalene (BEDT-TTF or ET) has made rapid progress during the past few years, recently culminating in the discovery of the ambient-pressure superconductors κ-(ET)$_2$Cu(NCS)$_2$$^{1)}$ and κ-(ET)$_2$Cu[N(CN)$_2$]X (X=CN, Br)$^{2,3)}$ with critical temperatures T_c as high as 10.4, 11.2, and 11.5 K, respectively. While T_c and other important characteristics such as the upper critical field H_{c2} and the critical current density $j_c$$^{4)}$ make the title compound attractive for application-oriented investigation, studies of this kind, except those devoted to the manufacturing of thin films,$^{5,6)}$ have been hampered as microcrystalline κ-(ET)$_2$Cu(NCS)$_2$ could only be obtained by grinding electrochemically grown crystals.$^{7)}$ Anodic electrocrystallization,$^{8)}$ the most common procedure$^{9)}$ for the preparation of superconducting radical cation salts has proven its usefulness for the generation of high-quality single crystals of κ-(ET)$_2$Cu(NCS)$_2$ needed for physical investigations,$^{10)}$ but is methodically restricted to very timeconsuming microscale batches and thus not a suitable method for the preparation of larger amounts of material. The lack of a convenient bulk-synthesis for microcrystalline κ-(ET)$_2$Cu(NCS)$_2$ prompted us to develop a new, nonelectrochemical preparation method for this salt.

Results and Discussion

Synthesis. Based on the well-known fact that Cu(SCN)$_2$ decomposes readily on heating to CuSCN, a redox reaction (formally) according to Eq. 1 was chosen as a promising approach.

$$2\ \overset{0}{\text{BEDT-TTF}} + \overset{+2}{\text{Cu(SCN)}_2} \xrightarrow[\Delta E]{\text{solvents}} \kappa\text{-}(\overset{+0.5}{\text{BEDT-TTF}})_2\ \overset{+1}{\text{Cu(NCS)}_2} \tag{1}$$

Suspended ET and Cu(SCN)$_2$ reacted indeed upon heating for 1 h in solvents like THF, benzonitrile or acetonitrile (method A),$^{11)}$ to give microcrystalline brown-black powders. Samples produced in the latter solvent were repeatedly contaminated with unreacted ET and tiny, white conglomerates as detected by visual inspection, whereas THF and benzonitrile gave much better results with respect to the presence of macroscopic impurities. Scanning electron microscopy (SEM) showed that products generated in acetonitrile consisted of elongated hexagonal platelet-like microcrystals partially embedded in an insulating matrix, the use of THF and benzonitrile yielded samples of similar appearance but enhanced homogeneity. The crystal morphology (cf. Fig. 1) resembled that found in electrochemically grown single crystals.$^{12)}$ As both reactants are only sparingly soluble in organic solvents it is difficult to achieve a homogenous reaction mixture by heating/stirring. This might account for side reactions like thermal degradation of Cu(SCN)$_2$ to CuSCN (particularly in acetonitrile) and thus for the observed incomplete conversion.

Upon modifying the conditions, it turned out that the reaction proceeded also quickly (30 min) in the cavity of an ultrasonic bath at room temperature (method B). Especially noteworthy is the fact that redox-reaction and crystal formation are initiated by soundwaves, since a mixture of the reactants remained unchanged for at least 36 h without the application of ultrasound. In contrast to method A, samples of κ-(ET)$_2$Cu(NCS)$_2$ obtained via this *sonochemical* route comprised more or less uniformly shaped hexagonal platelets and were of significantly increased homogeneity with respect to (insulating) impurities and grain size distribution as checked by SEM; a SEM image of a typical batch is displayed in Fig. 2.

In this context it should also be noted that attempts to carry out the redox process as a solid-phase reaction by annealing ET and Cu(SCN)$_2$ at temperatures ranging from 60—120°C have been unsuccessful so far. Experiments to obtain the title compound by oxidation of ET with dissolved (n-Bu$_4$N)$_2$[Cu(SCN)$_4$] according to method A or B failed likewise.

Characterization. FT-IR transmission spectroscopy was chosen for an initial product characterization. This method has been shown to be a powerful tool in the investigation of organic metals$^{13)}$ and offers, be-

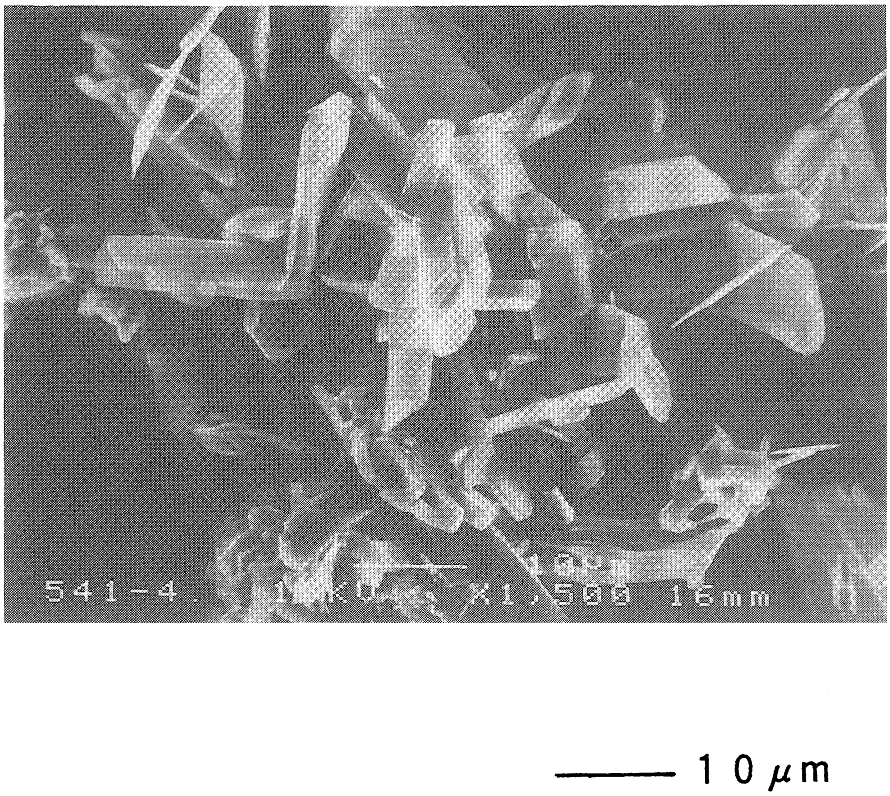

Fig. 1. SEM image of κ-(ET)$_2$Cu(NCS)$_2$ crystals prepared according to method A in THF.

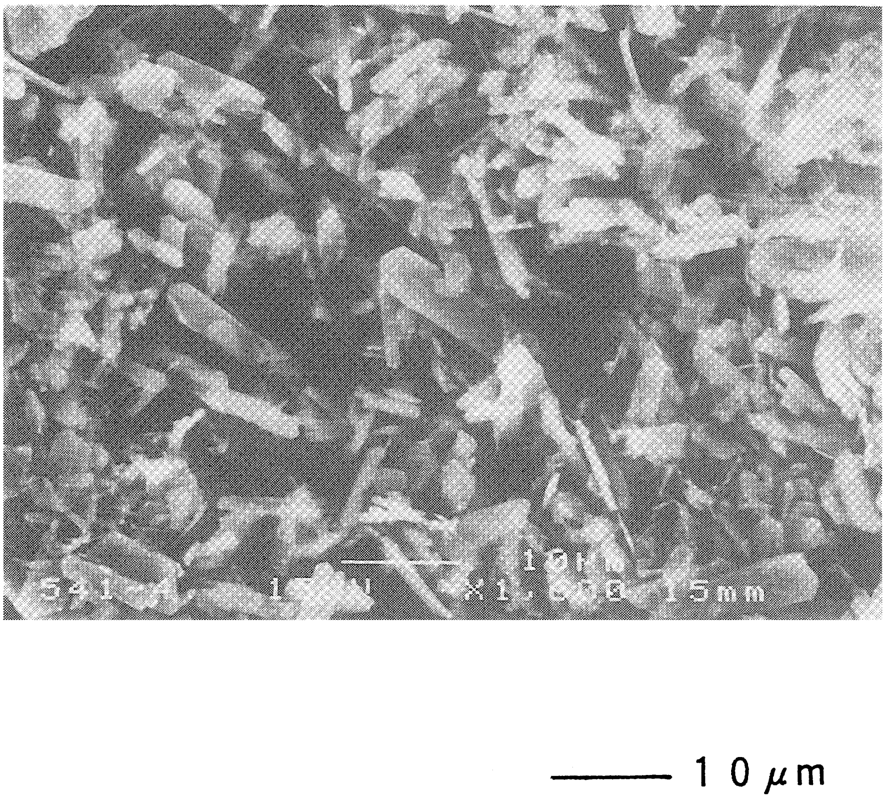

Fig. 2. SEM image of κ-(ET)$_2$Cu(NCS)$_2$ crystals prepared according to method B in THF.

sides the comparison of characteristic, fingerprint-type patterns, sensitive detection and identification of impurities. Thus, IR-spectroscopy provides a comparatively simple method to screen sample quality and purity with respect to contaminants like CuSCN, or less likely, unreacted starting compounds. The CN stretch vibrations of CuSCN and Cu(SCN)$_2$ appear at 2156 and 2147 cm^{-1}, respectively, whereas the Cu(NCS)$_2^-$-anion of κ-(ET)$_2$Cu(NCS)$_2$ gives rise to a sharp doublet at 2111 and 2068 cm^{-1}.[13] Identification of neutral ET besides the radicalic donor species is less straightforward, however, a sharp band at 771 cm^{-1}, unambiguously indicates the presence of unreacted donor.

B-samples, generated in THF or benzonitrile, exhibit characteristic features already described for authentic κ-(ET)$_2$Cu(NCS)$_2$ in the literature,[13] i. e. a broad electronic absorption ranging from 4000 to approximately 1500 cm^{-1}, a fingerprint-like feature caused by CN stretching modes of the anions[14] around 2100 cm^{-1}, followed by a pronounced vibronic pattern which starts around 1500 cm^{-1}. Spectra of sono- and electrochemically generated powders are virtually superimposable (cf. Fig. 3), thus indicating the formation of the title compound via method B. Similar results were obtained for thermally produced samples, albeit a weak band at 2156 cm^{-1} attributable to contamination by CuSCN was occasionally found for powders obtained in THF. Whereas the use of benzonitrile yielded samples containing traces of unreacted ET, this can be concluded from the appearance of a weak band at 771 cm^{-1}. Reactions carried out in acetonitrile according to method A or B gave comparatively poor results, since the so-obtained products still contained traces of donor as well as CuSCN; moreover an additional band at 2174 cm^{-1} was found for A-samples whose assignment is not yet clear.[15,16] It should be noted that bands due to unreacted Cu(SCN)$_2$ could neither be detected in A- nor in B-samples. Based on a semiquantitative IR analysis, the average sample purity of B-samples prepared in THF or benzonitrile is assumed to be better than 97% with respect to CuSCN, whereas the CuSCN-content of A-samples was estimated to be less than 6% (THF) or larger than 10% (acetonitrile). This matches well the results obtained by elemental analyses: Sonochemically prepared samples gave satisfactory values only when THF or benzonitrile were used as solvents; satisfactory *C* and *N* values could not be obtained for A-samples. In this context it should be noted that the purity of *microcrystalline* bulk material generated via method B (or A) cannot be expected to compete with that known for *single crystals* obtained by classical methods like galvanostatic electrocrystallization; this is mainly due to the fact that our procedure cannot take advantage of the efficient purification effect which is of considerable importance in any electrodeposition or electrocrystallization process. Since the use of THF gave by far the best results for both methods with respect to purity and yield, the following discussion will be restricted to products obtained using this solvent unless specified otherwise.

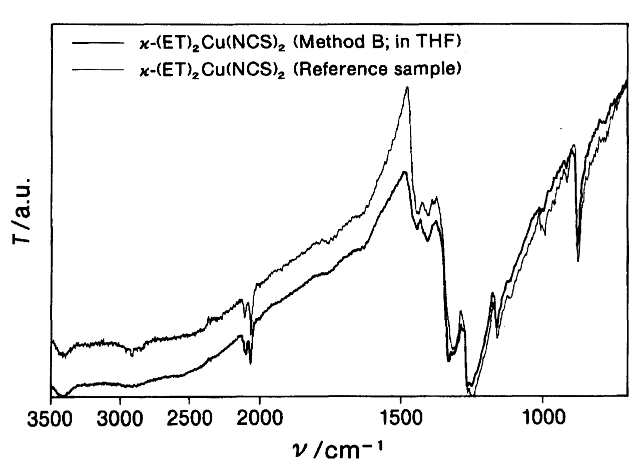

Fig. 3. IR transmission spectra of κ-(ET)$_2$Cu(NCS)$_2$. Thick solid line: Sonochemically prepared sample (method B). Thin solid line: Electrochemically grown reference sample.

The general appearance of ESR signals observed for A- and B-samples, is similar for both methods; typical spectra are displayed in Fig. 4. A- and B-samples exhibit symmetrical signals of Lorentzian shape, which consist of two superimposed signals, respectively: A broad one with a line-width $\Delta H = 63$ G (60 G) and a sharp one with $\Delta H = 14$ G (15 G) for A-samples (B-samples); precise linewidths were determined by computer simulation. The narrow line is much more pronounced for sonochemically than for thermally produced powders; in fact the signal shape of A-samples comes close to that of powdered, authentic κ-(ET)$_2$Cu(NCS)$_2$ which comprises a single line with $\Delta H \cong 67$ G. All samples revealed g-factors ranging between 2.001 (broad signal) and 2.002 (narrow signal) which differ markedly from the value expected for Cu^{2+}-ions (2.05—2.5)[17] and are similar to those found for the reference sample (g-factor=2.001). Thus, the presence of paramagnetic impurities due to the use of Cu^{II}(SCN)$_2$ and their well-known detrimental effect on superconductivity seems very unlikely. The ESR signal intensity amounts for A- and B-samples (determined for the superimposed signal) to approximately 2.19×10^{23} and 1.61×10^{23} spins/mol, respectively; for authentic material values ranging from 1.9×10^{23} to 2.09×10^{23} spins/mol were found. The intensities of the narrow signals are low and reach about 0.6% (A-sample) and 1.2% (B-sample) of the values found for the broad signals. These data indicate a high content of radicalic species in sonochemically and thermally produced samples and thus a complete conversion of the starting compounds. The lower spin concentration found for A-samples might hint to the presence of considerable amounts of diamagnetic impurities like CuSCN. Such a conclusion is somewhat questionable, however, because the experimental error of our measurements is rather high (ca. 30%) due to the use of $CuSO_4$ as standard for the calibration of the signal intensity.

Previous studies of electrochemically grown single crystals of κ-(ET)$_2$Cu(NCS)$_2$ described a single line with linewidths of approximately 61 G,$^{18)}$ 60—70 G$^{19)}$ or 26 G$^{20)}$ at room temperature. The signal with ΔH around 60 G can tentatively be assigned to the conduction electrons of κ-(ET)$_2$Cu(NCS)$_2$, whereas the additional, narrow signal observed for our samples, is not easily explicable unless one assumes the presence of two different phases. Interestingly, Urayama et al.$^{18)}$ reported a feature comprising two lines ($\Delta H \cong 100$ G and $\Delta H \cong 10$—20 G), albeit only at temperatures below 30 K, a behaviour not unsimilar to that found for A- and B-samples at ambient temperature. The appearance of a sample dependent, additional signal has been attributed to crystal imperfections by these authors, though the presence of a different phase was not ruled out with regard to the inconsistent values reported for ΔH in the literature.$^{21)}$

In this context it is noteworthy that an ESR feature, comprising two lines of widely differing widths has been found for mixed crystals of α- and β-(ET)$_2$I$_3$.$^{22)}$ In contrast to the present case, however, the linewidths measured for that system could readily be identified as a superposition of the signals of two well-characterized compounds. Moreover, the interpretation of ESR data was ascertained by X-ray studies and fully consistent with other physical characteristics. As regards to our samples, however, we think this phenomenon originates rather in crystal defects than in the presence of a (yet unidentified) additional phase; to date two nonsuperconducting phases α-(ET)$_2$Cu(NCS)$_2$$^{23)}$ and (ET)Cu$_2$(NCS)$_3$$^{24)}$ are known besides κ-(ET)$_2$Cu(NCS)$_2$, the linewidths of which amount to 60 and 7 G, respectively. Obviously, ΔH of neither compound matches with the signal in question ($\Delta H = 14$—15 G) observed for A- and B-samples.

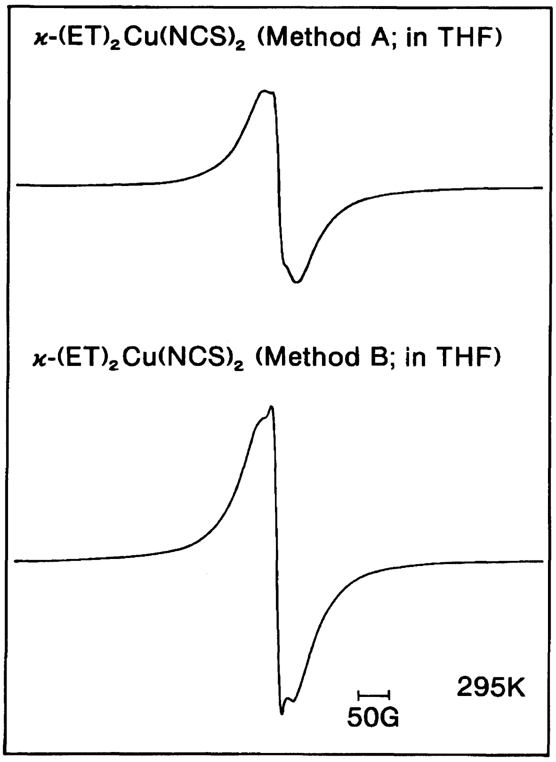

Fig. 4. ESR spectra of κ-(ET)$_2$Cu(NCS)$_2$. Upper panel: Thermally prepared sample (method A). Lower panel: Sonochemically prepared sample (method B).

By contrast, the assumption of a considerable concentration of defects does not seem unlikely when taking into account the fact that our data were obtained for (polycrystalline ?) microcrystals, grown under relatively drastic conditions compared to those of electrocrystallization experiments. On the other hand, the observed feature could also indicate a marked dependence of the ESR signal shapes on the preparation method employed. This interpretation is corroborated by the results of Gärtner et al.,$^{20)}$ who observed a linewidth of 26 G for κ-(ET)$_2$Cu(NCS)$_2$, prepared under potentiostatic conditions, as well as by a recent study of Awano et al.$^{6)}$ who described ESR spectra consisting of two lines ($\Delta H \cong 50$ and 20 G, respectively) for electrochemically deposited films of the title compound, the shapes of which resemble those shown in Fig. 4. It also deserves mentioning in this context that the pronounced influence of the preparation method on other physical properties (e.g. critical temperature T_c) of κ-(ET)$_2$Cu(NCS)$_2$ has been demonstrated earlier.$^{10)}$ However, a comparative ESR study, necessary to clarify the discrepancies of the linewidths reported in the literature, as well as the experimental finding outlined above, has not yet been performed.

For a further characterization of products obtained via method A or B, powder X-ray diffractograms (XRD) again employing electrochemically generated single crystals as reference, were recorded. Figures 5a and 5b (upper and middle panel) show the XRD patterns of the starting compounds ET and Cu(SCN)$_2$, Fig. 5c (undermost panel) refers to the initial, stoichiometric mixture of ET/Cu(SCN)$_2$ which was used as a starting material for both methods. The patterns displayed in Figs. 6a and 6b (upper and middle panel) correspond to samples prepared according to A and B (in THF), respectively; the undermost panel (Fig. 6c) refers to *oriented*, electrochemically produced single crystals mounted on a glass-substrate with the platelet-(b-c)-planes parellel to the glass surface. Since ET and Cu(SCN)$_2$ do not react at room temperature, Fig. 5c represents a superposition of the corresponding patterns of the single components. Hence, a comparison of Fig. 5c with Fig. 6 clearly indicates the disappearance of the reflections due to the starting compounds as will as

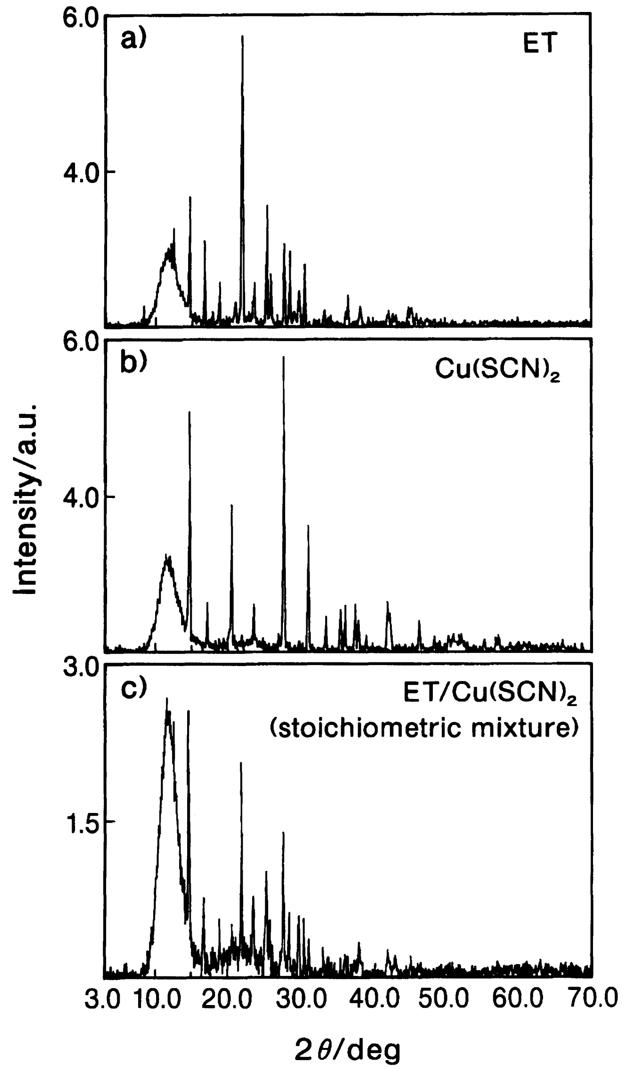

Fig. 5. X-Ray diffraction patterns of: a) ET. b) Cu(SCN)$_2$. c) Stoichiometric mixture of ET/Cu(SCN)$_2$.

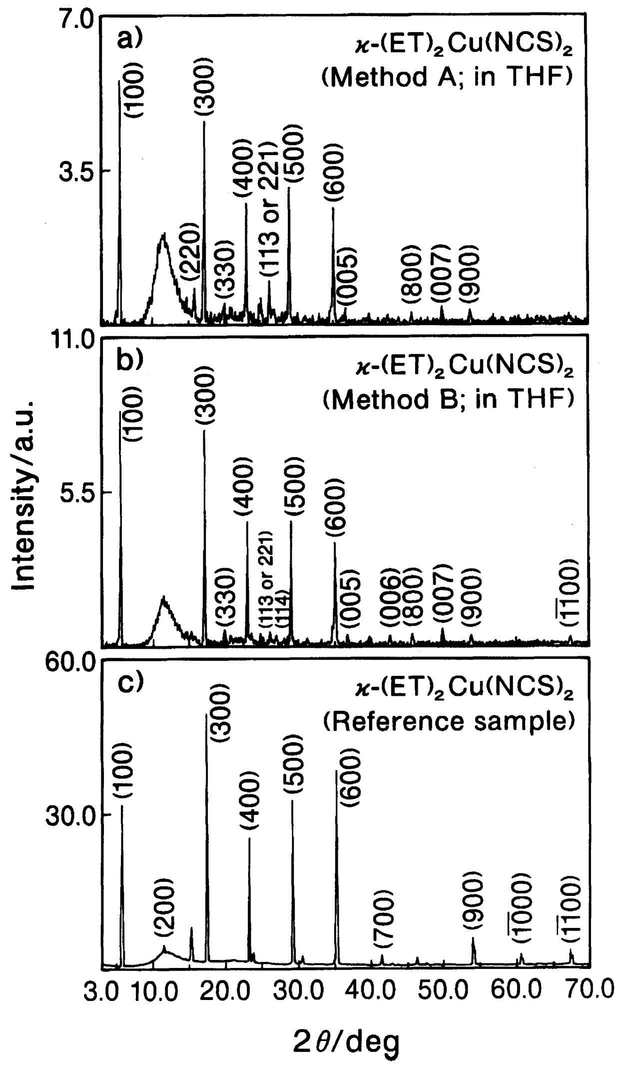

Fig. 6. X-Ray diffraction patterns of κ-(ET)$_2$Cu(NCS)$_2$ samples with a tentative assignment of observed reflections. a) κ-(ET)$_2$Cu(NCS)$_2$ prepared according to method A. b) κ-(ET)$_2$Cu(NCS)$_2$ prepared according to method B. c) Electrochemically grown crystals of κ-(ET)$_2$Cu(NCS)$_2$.

the formation of the desired product after a thermal or ultrasonic treatment. Comparison of the standard and samples reveals the virtual absence of strong reflections for $kl \neq 0$ and points to *preferred* rather than *random* orientation of the microcrystalline powders. The extremely broadened signals (centered at $2\theta \cong 11$ deg) are caused by silicon grease/glass substrates which were used for mounting the powder and hide the corresponding 200 reflection observed for the standard. The strong reflections observed for A- and B-samples (cf. Figs. 6a and 6b) can readily be assigned to $h00$ ($h=1$—6) reflections and agree well with those observed for the *oriented* reference sample. The remaining signals of low intensity, the assignment of which is somewhat tentative and not always unambiguous, can be attributed to reflections of *randomly* oriented microcrystals. This assignment could be ascertained by a comparison with the XRD patterns of *randomly* orientated authentic material. Within experimental accuracy signals due to unreacted starting compounds could not be detected which is in accordance with the results of IR and ESR spectroscopy mentioned above. Accurate identification of other contaminants, particularly of CuSCN, is difficult, since several bands of this possible impurity coincide accidentally with reflections of the product. The lines denoted with 113 (or 221) and 330 in Figs. 6a and 6b for instance, could be caused by κ-(ET)$_2$Cu(SCN)$_2$ as well as by CuSCN; the latter assignment would also hint to a higher CuSCN-content in A-samples and thus explain the observed intensity difference of the corresponding signals of A- and B-samples. Such an assumption, however, is highly speculative as none of the known, strong reflections of CuSCN[25)] could be observed and any intensity contribution of κ-(ET)$_2$Cu(SCN)$_2$ is completely neglected. The coincidence of the signals in question was confirmed by recording XRD patterns of authentic κ-(ET)$_2$Cu(NCS)$_2$ containing a defined amount of CuSCN (8%). Although the qualitative identification of this known impurity besides the desired product was possible, quantitative determination of the CuSCN content would require the absence of *preferred* orientation,[26)] a prerequisite no fulfilled in the present case. Similarly, it remains unclear, whether A- and B-samples contain small amounts (ca. 1—2%) of a different phase, which might be responsible for the narrow ESR line; an attribution of this line to significant amounts of amorphous components, as suggested by Awano et al.,[6)] is precluded by the good diffraction quality of our samples. Even though the presence of CuSCN and/or an unknown phase within our detection limit (assumed: 2—3%) cannot be ruled out completely, it should be stressed that there is no compelling need for such an assumption, as virtually all of the observed signals can be attributed to reflections of κ-(ET)$_2$Cu(SCN)$_2$, too. In fact, the poor intensity of the signals in question, particularly in the case of B-samples, strongly favours the presence of a single phase of considerable purity. Moreover, the excellent agreement of the (intensive) signals of standard and samples gives another independent proof for the bulk formation of the desired κ-(ET)$_2$Cu(NCS)$_2$.

Susceptibility measurements showed a superconducting transition with an onset temperature around 10 K (±1 K) for all samples obtained via A or B (regardless of the solvent employed), which confirms the formation of the title compound in both procedures; T_c is in good accordance with values reported previously for single crystals.[1,10)] Typical ZFC (Zero Field Cooled or shielding) and FC (Field Cooled or Meissner) curves of a sonochemically prepared powder (in THF) are depicted in Fig. 7. The shielding susceptibility χ_s *nominally* corresponds (at 5.7 K and 10 G for an assumed density ρ=1.7 g cm^{-3} and a zero demagnetization factor) to ca. 12% of the value for an ideal superconductor ($-1/4\pi$). This value is typical of samples generated in THF (or benzonitrile) according to method A or B. This seems to suggest that only a small volume fraction of the samples is actually superconducting since the shielding volume susceptibility of an ideal diamagnet is defined as 100%. However, in the case of small grains the penetration of the applied magnetic field H into a surface layer of thickness λ (the magnetic penetration depth) leads to a significant reduction of the observed magnetic moment.[27)] In the present samples typical grain sizes were estimated by SEM to ca. 40×10×1μm^3 (method A) and 10×2×0.5μm^3 (method B), whereas λ (T=0) is approximately 0.75 μm within the platelet plane[28)] and can be expected to be considerable larger in the perpendicular direction. Taking into consideration the random orientation of the microcrystals with respect to the magnetic field as well, we think that the observed incomplete shielding is still compatible with bulk superconductivity in these polycrystalline materials as had been found for large single crystals.[29)] Analogous effects have been described lately for microcrystalline samples of C$_{60}$-based superconductors.[30)]

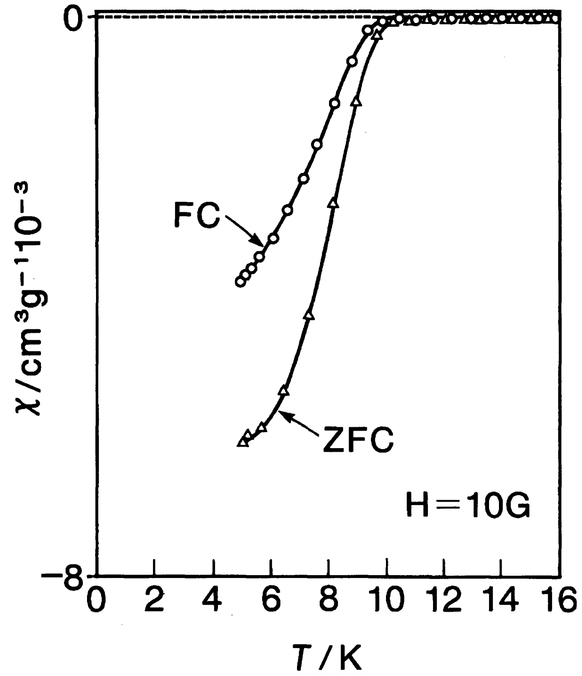

Fig. 7. DC-susceptibility of sonochemically prepared κ-(ET)$_2$Cu(NCS)$_2$ vs. temperature (upper curve: FC; lower curve: ZFC).

From the FC data there is clear evidence for the expulsion of incorporated magnetic flux (Meissner effect); the curve shown in Fig. 7 corresponds to a Meissner fraction of *nominally* 55% for a B-sample prepared in THF. Meissner fractions around 50 (±5) % were *reproducibly* found for microcrystalline powders generated in THF (or benzonitrile) regardless of the preparation method employed; once even values as high as 67% (A-sample; THF) and 90% (B-sample; benzonitrile) were observed, although their reproducibility proved difficult. These relatively high values corroborate the volume nature of the superconducting state and may also indicate very weak flux pinning and hence high purity of the material. The observed variation of the Meissner fraction might be a consequence of varying grain size distribution dependent of the method employed as well as on the individual batch. It should be emphasized, however, that with randomly orientated grains and the typical microcrystal being about the size of the current system of a single flux line, the physical situation is rather complicated and does not lend itself easily to simple conclusions regarding the ratio of Meissner to shielding susceptibilities.

In conclusion we have presented a new preparative pathway to the organic superconductor κ-(ET)$_2$Cu(NCS)$_2$ which is based on the redox reaction of ET and Cu(SCN)$_2$. Especially noteworthy is the fact that the reactants readily form the title compound as a microcrystalline powder upon ultrasound agitation at room-temperature in yields comparable to those of electrocrystallization experiments,[31] thus giving rise to the first *sonochemical* synthesis of an organic superconductor. In contrast to electrochemical crystal growth, which yields mg-amounts of high quality single crystals after 1—3 weeks of electrolysis, our procedure allows for an easy scale-up and provides a convenient and time-saving alternative to electrocrystallization experiments, whenever microcrystalline material is needed for application-oriented research.

Experimental

BEDT-TTF (Tokyo Kasei) and all dried solvents were used as purchased. Reference samples of κ-(ET)$_2$Cu(NCS)$_2$ were prepared according to the literature procedures.[1] All experiments were performed in an argon atmosphere.

IR-spectra were run on a Perkin–Elmer FT-IR 1600 spectrometer as KBr discs (64 or 640 repetitive scans). A semiquantitative IR analysis was carried out as previously described;[32] mixtures of authentic κ-(ET)$_2$Cu(NCS)$_2$ and CuSCN were used as standard samples.

ESR spectra were performed with a JEOL REIX (X-band, 9.4 GHz) spectrometer.

X-Ray diffractograms were recorded with a Rigaku Ru-300 diffractometer (Cu target, 45 kV, 260 mA, scan speed 12 deg min^{-1}), DC-susceptibility measurements were performed with the help of a Hoxan HS-SM 2000 SQUID-magnetometer equipped with a ^{4}He flow cryostat.

Cu(SCN)$_2$.[33] A saturated solution of KSCN (19.43 g; 0.2 mol) in water was added slowly to a precooled (0°C) solution of $\mathrm{CuSO_4 \times 5H_2O}$ (24.96 g; 0.1 mol) in 15% sulfuric acid dropwise under cooling (ice/water). The black precipitate was washed with icecold water (3×50 ml), ether (3×50 ml) and finally dried in vacuo. Yield: 11.6 g (65%). Found: C, 13.39; N, 15.60%. Calcd for $\mathrm{C_2N_2S_2Cu}$: C, 13.49; N, 15.60%. IR (KBr): 2147.4 (vs) and 744 (w) cm^{-1}.

(n-Bu$_4$)$_2$[Cu(SCN)$_4$].[34] A solution of KSCN (1.62 g; 16.7 mmol) in water (20 ml) was added dropwise to a suspension of Cu(SCN)$_2$ (1.5 g; 8.35 mmol) in cold water (ca. 100 ml, ice/water cooling bath). The resulting suspension was stirred for another 5 min and finally filtered into a stirred solution of n-Bu$_4$NBr (2.69 g; 8.35 mmol) in water (50 ml). The bright red precipitate formed was filtered off, washed with water (3×20 ml), dried in vacuo and finally reprecipitated from acetone/tetrachloromethane.

Yield: 1.15 g (19.3%) purple red crystals which decompose readily at room temperature but can be stored at +4°C for some weeks. Mp 83—84°C (melting under decomposition). Found: C, 55.26; H, 8.92; N, 11.26%. Calcd for $\mathrm{C_{36}H_{72}N_6S_4Cu}$: C, 55.38; H, 9.29; N, 10.76%. IR (KBr) 2962 (s), 2875 (m), 2086 (vs), 1470 (m), 1380 (w), 883 (w), 737 (w), and 473 (w) cm^{-1}.

κ-(ET)$_2$Cu(NCS)$_2$ (Method A).[35] BEDT-TTF (50 mg; 1.3×10^{-4} mol) and Cu(SCN)$_2$ (11.7 mg; 0.65×10^{-4} mol) are suspended in a dry solvent (e.g. THF, ca. 30 ml, water content $\ll$0.1%) and heated under stirring to reflux temperature (for benzonitrile: 80°C, oil bath temperature) for 1 h. The dark precipitate is filtered off, washed with the solvent used for the reaction, dry ether (2×10 ml) and dried in vacuo. Yield: 37.6 mg (61%) of a brown-black powder. Found: C, 26.19; H, 1.34; N, 3.94%. Calcd for $\mathrm{C_{22}H_{16}N_2S_{18}Cu}$: C, 27.84; H, 1.69; N, 2.95%.

When acetonitrile was used as solvent, white macroscopic impurities were removed before the analysis was performed. Found: C, 28.52; H, 1.79; N, 3.05%. Calcd for $\mathrm{C_{22}H_{16}N_2S_{18}Cu}$: C, 27.84; H, 1.69; N, 2.95%.

κ-(ET)$_2$Cu(NCS)$_2$ (Method B).[35] A suspension of the reactants prepared identically as described for A was placed in the waterfilled cavity of an ultrasonic bath (Branson 1200, Yamato) and agitated for 30 min at room temperature (21°C). The precipitate was filtered off and treated as described above. Yield: 40.0 mg (65%) of a homogeneous brown-black powder. Found: C, 27.53; H, 1.39; N, 3.10%. Calcd for $\mathrm{C_{22}H_{16}N_2S_{18}Cu}$: C, 27.84; H, 1.69; N, 2.95%.

When benzonitrile was used as a solvent the isolation of the product/removal of solvent proved difficult; hence the amounts of isolable product were significantly lower. Yield: 12.9 mg (21%). Found: C, 27.66; H, 1.51; N, 3.24%. Calcd for $\mathrm{C_{22}H_{16}N_2S_{18}Cu}$: C, 27.84; H, 1.69; N, 2.95%.

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