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# Synthesis and crystal structure of $[Mo_3S_7(S_2CNEt_2)_3]_2(TCNQ)_2$; salt of a radical anion and a cluster cation

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## Abstract

$[Mo_3S_7(dtc)_3]dtc$ (dtc = $S_2CNEt_2$) reacts with one or more equivalents of TCNQ (7,7,8,8-tetracyanoquinodimethane) in $CH_3CN$ to form radical-anion salts $[Mo_3S_7(dtc)_3]_2(TCNQ)_2$ (**1**) and $[Mo_3S_7(dtc)_3](TCNQ)_2$ (**2**), respectively. By an analogous method from $[Mo_3Se_7(dtc)_3]dtc$ the seleno complex $[Mo_3Se_7(dtc)_3](TCNQ)_2$ (**3**) was obtained. The structure of **1** was established by X-ray structural analysis. The crystals are orthorhombic, space group *Pbca*, $a = 24.388(4)$, $b = 14.043(2)$, $c = 25.224(6)$ Å. The structure has been solved to $R_F$ 0.049. The geometry of the $[Mo_3S_7(dtc)_3]^+$ cation is normal; the most interesting feature of the structure is the presence of rather short contacts between N atoms of TCNQ and S atoms of $S_2$ ligands of the cation (the S...N distances are 2.91–2.95 Å). The TCNQ anions form centrosymmetrical dimers (the separation between the corresponding planes is 3.16 Å), so the formula of **I** can be written as $[Mo_3S_7(dtc)_3]_2(TCNQ)_2$.

## Introduction

7,7,8,8-Tetracyanoquinodimethane (TCNQ) is widely used for the preparation of charge-transfer complexes and radical-ion salts which often show metallic conductivity and other interesting properties [1]. Salts of TCNQ with complex cations [2–6] form a special group among numerous known complexes. However, only a few examples are known where these cations are cluster ones, such as $[Nb_3Cl_6(\eta^6\text{-}C_6Me_6)_3](TCNQ)_2$ [7] and salts of the type $[M_4Y_4Cp_4](TCNQ)_n$ (M = Mo, Cr, Fe; Y = S, Se; $n = 1, 2$) [8]. In such compounds the nature of the cation determines the way of packing in the crystal and there are interesting cation–anion interactions. In the present work we report the reaction of the triangular clusters $Mo_3Y_7(dtc)_4$ (Y = S, Se) with TCNQ and the crystal structure of $[Mo_3S_7(dtc)_3]_2(TCNQ)_2$.

## Experimental

All reactions were carried out in air. $CH_3CN$ and $CH_2Cl_2$ were distilled over $P_4O_{10}$. $Mo_3S_7(dtc)_4$ and $Mo_3Se_7(dtc)_4$ were prepared according to published methods [9, 10]. TCNQ (CHEMAPOL) was sublimed before using. Determination of C, H and N was performed in the Laboratory of Microanalysis of the Institute of Organic Chemistry (Novosibirsk). Mo and S were determined gravimetrically as $MoO_2(C_9H_6NO)_2$ and $BaSO_4$. IR spectra were recorded on a IR-75 spectrometer in KBr pellets. The effective magnetic moment was determined from magnetic susceptibility data by the relative Faraday method taking into account diamagnetism. ESR spectra were recorded on a Varian E-12 spectrometer.

### *Preparation of $[Mo_3S_7(dtc)_3]_2(TCNQ)_2$ (1)*

A suspension of $Mo_3S_7(dtc)_4$ (0.30 g, 0.25 mmol) was boiled with TCNQ (0.05 g, 0.25 mmol) in $CH_3CN$ in air for 30 min. The resultant green precipitate was filtered off and washed with cold acetone. Purification occurred by dissolving the solid in $CH_2Cl_2$ and applying a layer of pentane. 0.24 g of complex $[Mo_3S_7(dtc)_3]_2(TCNQ)_2$ (**1**) was obtained. Yield 75%.

*Anal.* Calc. for $C_{54}H_{68}N_{14}Mo_6S_{26}$: C, 25.7; H, 3.0; Mo, 25.6; S, 37.1. Found: C, 25.4; H, 3.1; Mo, 25.4; S, 37.6%.

### *Preparation of $[Mo_3Y_7(dtc)_3](TCNQ)_2$ (Y = S, (2), Se (3))*

A suspension of $Mo_3S_7(dtc)_4$ (0.30 g, 0.25 mmol) was boiled with TCNQ (0.10 g, 0.5 mmol) in $CH_3CN$ in air for 30 min. The resultant green precipitate was filtered off, washed with cold acetone. Purification occurred by reprecipitating the solid from $CH_2Cl_2$ so-

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lution with pentane. 0.28 g of complex $[Mo_3S_7(dtc)_3](TCNQ)_2$ (**2**) was obtained. Yield 74%.

*Anal.* Calc. for $C_{39}H_{38}N_{11}Mo_3S_{13}$: C, 34.8; H, 1.3; N, 11.5; Mo, 21.4; S, 30.9. Found: C, 34.5; H, 2.0; N, 10.8; Mo, 21.2; S, 29.8%. ESR: $g = 2.003$ (solid, 290 K); $g = 2.004$ (solution in $CH_2Cl_2$). $\mu_{eff}$ 1.43 BM (290 K).

TABLE 1. Atomic coordinates and equivalent ($U_{eq}$) thermal parameters for non-hydrogen atoms of **1**

| | $x$ | $y$ | $z$ | $U^a$ |
|---|---|---|---|---|
| Mo(1) | 0.5955(1) | 0.2240(2) | 0.2618(1) | 0.032(2) |
| Mo(2) | 0.4888(1) | 0.2797(2) | 0.2678(1) | 0.033(2) |
| Mo(3) | 0.5541(1) | 0.3440(2) | 0.1877(1) | 0.031(2) |
| S(1) | 0.5263(3) | 0.1834(6) | 0.1995(3) | 0.038(7) |
| S(121) | 0.5304(3) | 0.1628(7) | 0.3298(3) | 0.041(7) |
| S(122) | 0.5549(4) | 0.2992(6) | 0.3374(3) | 0.035(6) |
| S(131) | 0.6492(3) | 0.2824(7) | 0.1848(3) | 0.048(7) |
| S(132) | 0.6325(3) | 0.3789(6) | 0.2426(3) | 0.042(6) |
| S(231) | 0.4542(4) | 0.3798(6) | 0.1935(3) | 0.043(6) |
| S(232) | 0.5030(4) | 0.4459(5) | 0.2469(3) | 0.041(6) |
| S(11) | 0.6290(4) | 0.0606(6) | 0.2452(3) | 0.039(6) |
| S(12) | 0.6788(4) | 0.1918(6) | 0.3173(4) | 0.046(7) |
| S(21) | 0.4060(3) | 0.1764(6) | 0.2598(3) | 0.039(6) |
| S(22) | 0.4173(4) | 0.3300(7) | 0.3338(4) | 0.050(7) |
| S(31) | 0.5472(4) | 0.3059(6) | 0.0931(3) | 0.056(7) |
| S(32) | 0.5754(4) | 0.4894(7) | 0.1339(3) | 0.053(7) |
| C(1) | 0.679(1) | 0.085(2) | 0.291(1) | 0.04(2) |
| C(2) | 0.376(1) | 0.243(2) | 0.308(1) | 0.02(2) |
| C(3) | 0.573(1) | 0.415(3) | 0.080(1) | 0.06(3) |
| N(1) | 0.710(1) | 0.016(2) | 0.306(1) | 0.04(2) |
| C(11) | 0.712(1) | −0.085(2) | 0.288(1) | 0.04(1) |
| C(12) | 0.695(2) | −0.156(3) | 0.329(1) | 0.07(1) |
| C(13) | 0.760(2) | 0.032(3) | 0.344(1) | 0.06(1) |
| C(14) | 0.739(2) | 0.032(3) | 0.400(1) | 0.08(1) |
| N(2) | 0.325(1) | 0.225(2) | 0.326(1) | 0.06(2) |
| C(21) | 0.299(1) | 0.289(3) | 0.366(1) | 0.06(1) |
| C(22) | 0.313(2) | 0.255(4) | 0.421(2) | 0.12(2) |
| C(23) | 0.288(2) | 0.159(3) | 0.298(1) | 0.07(1) |
| C(24) | 0.273(2) | 0.077(3) | 0.334(2) | 0.10(2) |
| N(3) | 0.588(2) | 0.442(2) | 0.032(1) | 0.12(3) |
| C(31) | 0.611(2) | 0.540(4) | 0.021(2) | 0.13(2) |
| C(32) | 0.574(3) | 0.594(5) | −0.002(3) | 0.28(3) |
| C(33) | 0.599(3) | 0.373(4) | −0.013(2) | 0.15(2) |
| C(34) | 0.645(3) | 0.334(4) | −0.008(2) | 0.16(2) |
| C(1T) | −0.022(1) | 0.084(2) | 0.435(1) | 0.005(7) |
| C(2T) | −0.010(2) | 0.124(2) | 0.486(1) | 0.04(1) |
| C(3T) | 0.040(2) | 0.113(2) | 0.509(1) | 0.04(1) |
| C(4T) | 0.084(2) | 0.071(2) | 0.485(1) | 0.04(1) |
| C(5T) | 0.075(1) | 0.031(2) | 0.432(1) | 0.04(1) |
| C(6T) | 0.024(1) | 0.037(2) | 0.411(1) | 0.04(1) |
| C(7T) | −0.072(1) | 0.095(2) | 0.408(1) | 0.026(9) |
| C(71T) | −0.084(1) | 0.047(2) | 0.360(1) | 0.04(1) |
| C(72T) | −0.112(2) | 0.157(3) | 0.427(2) | 0.06(1) |
| C(8T) | 0.135(2) | 0.063(3) | 0.507(2) | 0.06(1) |
| C(81T) | 0.180(2) | 0.019(3) | 0.481(2) | 0.07(1) |
| C(82T) | 0.150(2) | 0.104(3) | 0.558(2) | 0.06(1) |
| N(71T) | −0.086(1) | 0.001(2) | 0.325(1) | 0.06(2) |
| N(72T) | −0.146(2) | 0.202(3) | 0.445(1) | 0.10(3) |
| N(81T) | 0.220(2) | −0.008(3) | 0.457(1) | 0.11(3) |
| N(82T) | 0.160(1) | 0.135(2) | 0.600(1) | 0.06(2) |

[a] $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$. See Fig. 3 for atomic labelling scheme.

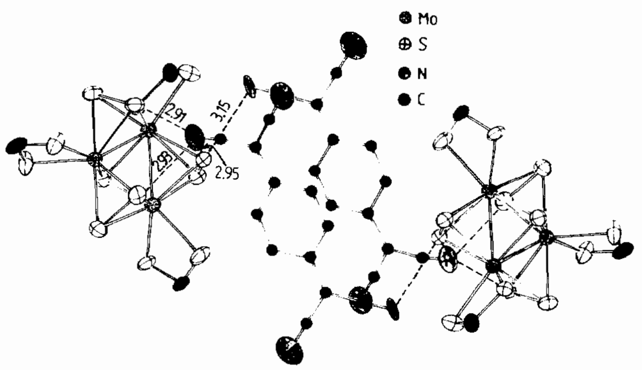

Fig. 1. $[Mo_3S_7(dtc)_3]_2(TCNQ)_2$ (**1**).

TABLE 2. Bond distances (Å) in **1**

| | | | |
|---|---|---|---|
| Mo(1)–Mo(2) | 2.720(4) | Mo(1)–Mo(3) | 2.711(4) |
| Mo(1)–S(1) | 2.375(9) | Mo(1)–S(121) | 2.490(9) |
| Mo(1)–S(122) | 2.393(8) | Mo(1)–S(131) | 2.481(9) |
| Mo(1)–S(132) | 2.404(9) | Mo(1)–S(11) | 2.471(9) |
| Mo(1)–S(12) | 2.51(1) | Mo(2)–Mo(3) | 2.726(4) |
| Mo(2)–S(1) | 2.372(8) | Mo(2)–S(121) | 2.482(9) |
| Mo(2)–S(122) | 2.397(9) | Mo(2)–S(231) | 2.491(9) |
| Mo(2)–S(232) | 2.418(8) | Mo(2)–S(21) | 2.494(9) |
| Mo(2)–S(22) | 2.512(9) | Mo(3)–S(1) | 2.373(9) |
| Mo(3)–S(131) | 2.475(9) | Mo(3)–S(132) | 2.409(9) |
| Mo(3)–S(231) | 2.49(1) | Mo(3)–S(232) | 2.414(9) |
| Mo(3)–S(31) | 2.453(8) | Mo(3)–S(32) | 2.506(9) |
| S(121)–S(122) | 2.02(1) | S(131)–S(132) | 2.03(1) |
| S(231)–S(232) | 2.02(1) | S(11)–C(1) | 1.71(3) |
| S(12)–C(1) | 1.64(3) | S(21)–C(2) | 1.70(3) |
| S(22)–C(2) | 1.70(3) | S(31)–C(3) | 1.69(4) |
| S(32)–C(3) | 1.71(4) | C(1)–N(1) | 1.28(4) |
| C(2)–N(2) | 1.35(4) | C(3)–N(3) | 1.34(5) |
| N(1)–C(11) | 1.49(4) | N(1)–C(13) | 1.56(4) |
| C(11)–C(12) | 1.48(5) | C(13)–C(14) | 1.50(5) |
| N(2)–C(21) | 1.48(5) | N(2)–C(23) | 1.49(5) |
| C(21)–C(22) | 1.51(6) | C(23)–C(24) | 1.51(6) |
| N(3)–C(31) | 1.51(6) | N(3)–C(33) | 1.51(7) |
| C(31)–C(32) | 1.31(9) | C(33)–C(34) | 1.25(9) |
| C(1T)–C(2T) | 1.43(4) | C(1T)–C(6T) | 1.43(4) |
| C(1T)–C(7T) | 1.42(4) | C(2T)–C(3T) | 1.35(5) |
| C(3T)–C(4T) | 1.37(5) | C(4T)–C(5T) | 1.45(5) |
| C(4T)–C(8T) | 1.38(5) | C(5T)–C(6T) | 1.36(5) |
| C(7T)–C(71T) | 1.40(5) | C(7T)–C(72T) | 1.40(5) |
| C(71T)–N(71T) | 1.12(4) | C(72T)–N(72T) | 1.13(6) |
| C(8T)–C(81T) | 1.42(6) | C(8T)–C(82T) | 1.45(6) |
| C(81T)–N(81T) | 1.19(6) | C(82T)–N(82T) | 1.16(5) |

By a similar method starting from $Mo_3Se_7(dtc)_4$ and TCNQ, $[Mo_3Se_7(dtc)_3](TCNQ)_2$ (**3**) was obtained in 67% yield.

*Anal.* Calc. for $C_{39}H_{38}N_{11}Mo_3S_6Se_7$: C, 27.3; H, 2.2; N, 9.4. Found: C, 27.6; H, 2.2; N, 9.1%. ESR: $g = 2.0030$ (solid, 290 K); $g = 2.0026$ (solid, 77 K).

### *X-ray structure determination*

The structure of **1** was determined by means of X-ray structural analysis, performed on a Syntex $P2_1$ diffractometer using the standard procedure ($\lambda Cu_{\alpha}$,

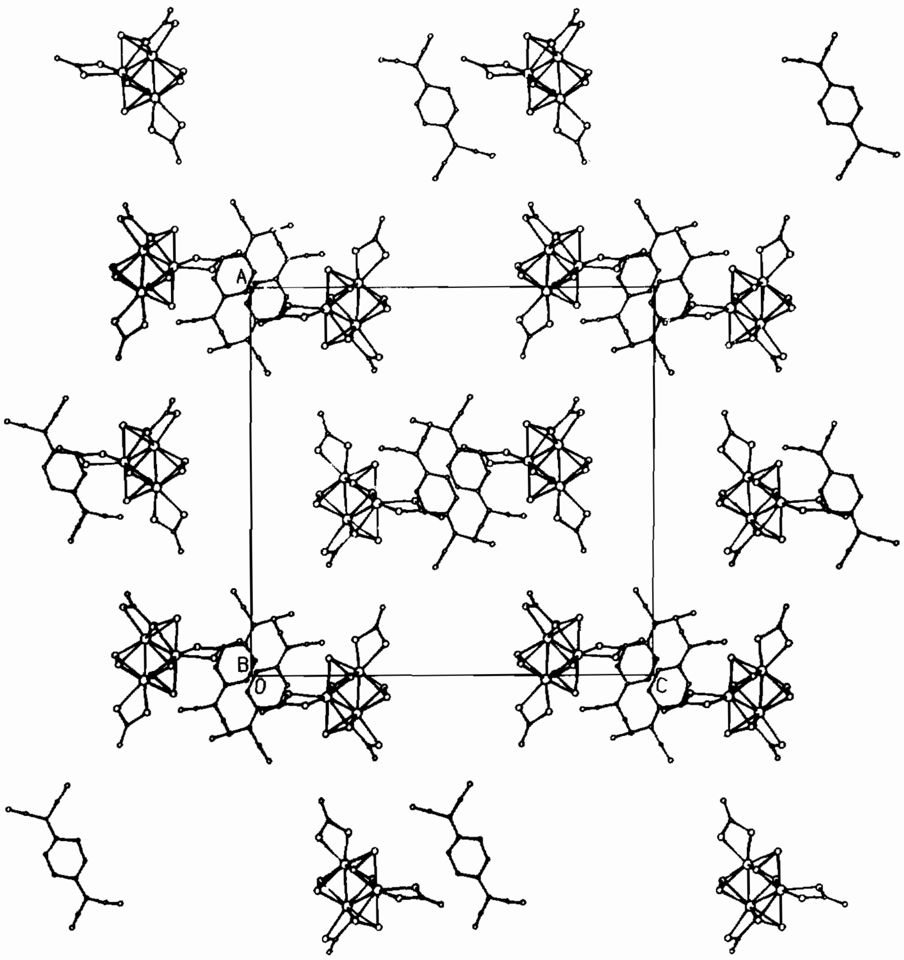

Fig. 2. View of an elementary cell of **1**; a projection on the *ac* plane.

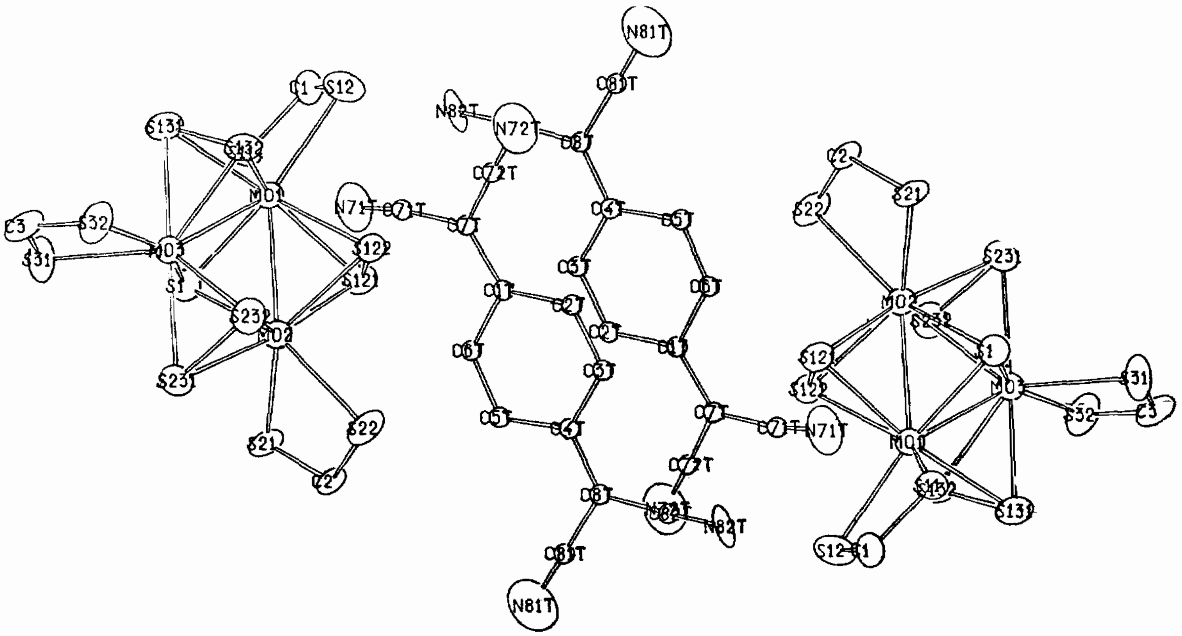

Fig. 3. Atomic labelling scheme for **1**.

TABLE 3. Bond angles (°) in **1**

| | | | |
|---|---|---|---|
| Mo(2)–Mo(1)–Mo(3) | 60.3(1) | Mo(2)–Mo(1)–S(1) | 55.0(2) |
| Mo(3)–Mo(1)–S(1) | 55.2(2) | Mo(2)–Mo(1)–S(121) | 56.7(2) |
| Mo(3)–Mo(1)–S(121) | 116.9(2) | S(1)–Mo(1)–S(121) | 85.4(3) |
| Mo(2)–Mo(1)–S(122) | 55.5(2) | Mo(3)–Mo(1)–S(122) | 96.9(2) |
| S(1)–Mo(1)–S(122) | 109.8(3) | S(121)–Mo(1)–S(122) | 48.7(3) |
| Mo(2)–Mo(1)–S(131) | 116.9(2) | Mo(3)–Mo(1)–S(131) | 56.7(2) |
| S(1)–Mo(1)–S(131) | 86.4(3) | S(121)–Mo(1)–S(131) | 171.6(3) |
| S(122)–Mo(1)–S(131) | 134.1(3) | Mo(2)–Mo(1)–S(132) | 96.3(2) |
| Mo(3)–Mo(1)–S(132) | 55.8(2) | S(1)–Mo(1)–S(132) | 110.5(3) |
| S(121)–Mo(1)–S(132) | 133.7(3) | S(122)–Mo(1)–S(132) | 85.2(3) |
| S(131)–Mo(1)–S(132) | 49.1(3) | Mo(2)–Mo(1)–S(11) | 126.3(2) |
| Mo(3)–Mo(1)–S(11) | 125.6(2) | S(1)–Mo(1)–S(11) | 84.2(3) |
| S(121)–Mo(1)–S(11) | 90.4(3) | S(122)–Mo(1)–S(11) | 133.0(3) |
| S(131)–Mo(1)–S(11) | 90.0(3) | S(132)–Mo(1)–S(11) | 133.0(3) |
| Mo(2)–Mo(1)–S(12) | 142.7(3) | Mo(3)–Mo(1)–S(12) | 143.0(2) |
| S(1)–Mo(1)–S(12) | 154.3(3) | S(121)–Mo(1)–S(12) | 94.0(3) |
| S(122)–Mo(1)–S(12) | 88.3(3) | S(131)–Mo(1)–S(12) | 94.0(3) |
| S(132)–Mo(1)–S(12) | 88.4(3) | S(11)–Mo(1)–S(12) | 70.1(3) |
| Mo(1)–Mo(2)–Mo(3) | 59.7(1) | Mo(1)–Mo(2)–S(1) | 55.1(2) |
| Mo(3)–Mo(2)–S(1) | 55.0(2) | Mo(1)–Mo(2)–S(121) | 57.0(2) |
| Mo(3)–Mo(2)–S(121) | 116.6(2) | S(1)–Mo(2)–S(121) | 85.6(3) |
| Mo(1)–Mo(2)–S(122) | 55.3(2) | Mo(3)–Mo(2)–S(122) | 96.4(2) |
| S(1)–Mo(2)–S(122) | 109.7(3) | S(121)–Mo(2)–S(122) | 48.8(3) |
| Mo(1)–Mo(2)–S(231) | 116.4(2) | Mo(3)–Mo(2)–S(231) | 56.8(2) |
| S(1)–Mo(2)–S(231) | 84.6(3) | S(121)–Mo(2)–S(231) | 170.2(3) |
| S(122)–Mo(2)–S(231) | 135.5(3) | Mo(1)–Mo(2)–S(232) | 97.4(2) |
| Mo(3)–Mo(2)–S(232) | 55.6(2) | S(1)–Mo(2)–S(232) | 109.6(3) |
| S(121)–Mo(2)–S(232) | 135.8(3) | S(122)–Mo(2)–S(232) | 87.3(3) |
| S(231)–Mo(2)–S(232) | 48.6(3) | Mo(1)–Mo(2)–S(21) | 127.0(2) |
| Mo(3)–Mo(2)–S(21) | 127.3(2) | S(1)–Mo(2)–S(21) | 85.5(3) |
| S(121)–Mo(2)–S(21) | 89.8(3) | S(122)–Mo(2)–S(21) | 132.0(3) |
| S(231)–Mo(2)–S(21) | 89.6(3) | S(232)–Mo(2)–S(21) | 131.3(3) |
| Mo(1)–Mo(2)–S(22) | 141.4(2) | Mo(3)–Mo(2)–S(22) | 143.4(3) |
| S(1)–Mo(2)–S(22) | 155.3(3) | S(121)–Mo(2)–S(22) | 93.0(3) |
| S(122)–Mo(2)–S(22) | 87.1(3) | S(231)–Mo(2)–S(22) | 96.0(3) |
| S(232)–Mo(2)–S(22) | 88.4(3) | S(21)–Mo(2)–S(22) | 69.8(3) |
| Mo(1)–Mo(3)–Mo(2) | 60.0(1) | Mo(1)–Mo(3)–S(1) | 55.2(2) |
| Mo(2)–Mo(3)–S(1) | 54.9(2) | Mo(1)–Mo(3)–S(131) | 57.0(2) |
| Mo(2)–Mo(3)–S(131) | 116.9(2) | S(1)–Mo(3)–S(131) | 86.5(3) |
| Mo(1)–Mo(3)–S(132) | 55.6(2) | Mo(2)–Mo(3)–S(132) | 96.0(2) |
| S(1)–Mo(3)–S(132) | 110.4(3) | S(131)–Mo(3)–S(132) | 49.1(3) |
| Mo(1)–Mo(3)–S(231) | 116.7(2) | Mo(2)–Mo(3)–S(231) | 56.8(2) |
| S(1)–Mo(3)–S(231) | 84.5(3) | S(131)–Mo(3)–S(231) | 171.1(3) |
| S(132)–Mo(3)–S(231) | 134.5(3) | Mo(1)–Mo(3)–S(232) | 97.7(2) |
| Mo(2)–Mo(3)–S(232) | 55.7(2) | S(1)–Mo(3)–S(232) | 109.8(3) |
| S(131)–Mo(3)–S(232) | 135.1(3) | S(132)–Mo(3)–S(232) | 86.2(3) |
| S(231)–Mo(3)–S(232) | 48.7(3) | Mo(1)–Mo(3)–S(31) | 124.1(3) |
| Mo(2)–Mo(3)–S(31) | 127.5(3) | S(1)–Mo(3)–S(31) | 84.0(3) |
| S(131)–Mo(3)–S(31) | 87.7(3) | S(132)–Mo(3)–S(31) | 131.1(3) |
| S(231)–Mo(3)–S(31) | 91.9(3) | S(232)–Mo(3)–S(31) | 134.1(3) |
| Mo(1)–Mo(3)–S(32) | 143.4(3) | Mo(2)–Mo(3)–S(32) | 142.4(2) |
| S(1)–Mo(3)–S(32) | 154.3(3) | S(131)–Mo(3)–S(32) | 94.3(3) |
| S(132)–Mo(3)–S(32) | 88.9(3) | S(231)–Mo(3)–S(32) | 94.0(3) |
| S(232)–Mo(3)–S(32) | 87.6(3) | S(31)–Mo(3)–S(32) | 70.4(3) |
| Mo(1)–S(1)–Mo(2) | 69.9(2) | Mo(1)–S(1)–Mo(3) | 69.6(2) |
| Mo(2)–S(1)–Mo(3) | 70.1(2) | Mo(1)–S(121)–Mo(2) | 66.3(2) |
| Mo(1)–S(121)–S(122) | 63.1(3) | Mo(2)–S(121)–S(122) | 63.4(3) |
| Mo(1)–S(122)–Mo(2) | 69.2(2) | Mo(1)–S(122)–S(121) | 68.1(3) |
| Mo(2)–S(122)–S(121) | 67.8(3) | Mo(1)–S(131)–Mo(3) | 66.3(2) |
| Mo(1)–S(131)–S(132) | 63.5(3) | Mo(3)–S(131)–S(132) | 63.8(3) |
| Mo(1)–S(132)–Mo(3) | 68.5(2) | Mo(1)–S(132)–S(131) | 67.4(4) |
| Mo(3)–S(132)–S(131) | 67.1(4) | Mo(2)–S(231)–Mo(3) | 66.3(2) |

*(continued)*

TABLE 3. (*continued*)

| | | | |
|---|---|---|---|
| Mo(2)–S(231)–S(232) | 63.8(3) | Mo(3)–S(231)–S(232) | 63.6(4) |
| Mo(2)–S(232)–Mo(3) | 68.7(2) | Mo(2)–S(232)–S(231) | 67.6(3) |
| Mo(3)–S(232)–S(231) | 67.7(4) | Mo(1)–S(11)–C(1) | 86(1) |
| Mo(1)–S(12)–C(1) | 87(1) | Mo(2)–S(21)–C(2) | 88(1) |
| Mo(2)–S(22)–C(2) | 87(1) | Mo(3)–S(31)–C(3) | 88(1) |
| Mo(3)–S(32)–C(3) | 86(1) | S(11)–C(1)–S(12) | 117(2) |
| S(11)–C(1)–N(1) | 118(2) | S(12)–C(1)–N(1) | 125(2) |
| S(21)–C(2)–S(22) | 115(2) | S(21)–C(2)–N(2) | 122(2) |
| S(22)–C(2)–N(2) | 123(2) | S(31)–C(3)–S(32) | 115(2) |
| S(31)–C(3)–N(3) | 122(3) | S(32)–C(3)–N(3) | 123(3) |
| C(1)–N(1)–C(11) | 130(3) | C(1)–N(1)–C(13) | 122(3) |
| C(11)–N(1)–C(13) | 107(2) | N(1)–C(11)–C(12) | 116(3) |
| N(1)–C(13)–C(14) | 109(3) | C(2)–N(2)–C(21) | 120(3) |
| C(2)–N(2)–C(23) | 121(3) | C(21)–N(2)–C(23) | 117(3) |
| N(2)–C(21)–C(22) | 110(3) | N(2)–C(23)–C(24) | 109(3) |
| C(3)–N(3)–C(31) | 122(3) | C(3)–N(3)–C(33) | 123(4) |
| C(31)–N(3)–C(33) | 114(4) | N(3)–C(31)–C(32) | 110(5) |
| N(3)–C(33)–C(34) | 111(5) | C(2T)–C(1T)–C(6T) | 114(3) |
| C(2T)–C(1T)–C(7T) | 124(3) | C(6T)–C(1T)–C(7T) | 121(2) |
| C(1T)–C(2T)–C(3T) | 121(3) | C(2T)–C(3T)–C(4T) | 125(3) |
| C(3T)–C(4T)–C(5T) | 117(3) | C(3T)–C(4T)–C(8T) | 125(3) |
| C(5T)–C(4T)–C(8T) | 118(3) | C(4T)–C(5T)–C(6T) | 118(3) |
| C(1T)–C(6T)–C(5T) | 125(3) | C(1T)–C(7T)–C(71T) | 123(3) |
| C(1T)–C(7T)–C(72T) | 121(3) | C(71T)–C(7T)–C(72T) | 117(3) |
| C(7T)–C(71T)–N(71T) | 169(4) | C(7T)–C(72T)–N(72T) | 175(4) |
| C(4T)–C(8T)–C(81T) | 123(3) | C(4T)–C(8T)–C(82T) | 123(3) |
| C(81T)–C(8T)–C(82T) | 113(4) | C(8T)–C(81T)–N(81T) | 173(4) |
| C(8T)–C(82T)–N(82T) | 177(4) | | |

$2\theta_{max}=85°$, $N_{meas}=3223$, correction for absorption by means of a $\psi$-curve). The crystals are orthorhombic, $a=24.388(4)$, $b=14.043(2)$, $c=25.224(6)$ Å, $V_{cell}=8639(3)$ Å$^3$, $D_{calc}=1.7$ g/cm$^3$, $Z=8$, space group *Pbca*, $R_F=0.049$ for 1392 ($F>6\sigma(F)$). The structure was solved by the direct method using the SHELX 86 program [11] and refined by full-matrix least-squares in the anisotropic approximation for all non-hydrogen atoms other than the carbons of the ethyl groups and TCNQ using the YANX package of programs [12]. The hydrogen atoms were placed into calculated position with $U_{iso}=0.08$ Å. The atomic coordinates are given in Table 1.

## Results and discussion

TCNQ shows moderate oxidative properties comparable with those of iodine or organic disulfides being reduced to a unicharged radical-anion [13]. It can also oxidize various neutral molecules. Thus, the $Co_3S(CO)_9$ cluster yields the $[Co_3S(CO)_9]^+$ cation under treatment with TCNQ in solution [14]. In our case only dithiocarbamate of the outer sphere was oxidized under the conditions of the reaction (eqn. (1))

$$2[Mo_3S_7(dtc)_3]dtc+2TCNQ=$$
$$[Mo_3S_7(dtc)_3]_2(TCNQ)_2+(dtc)_2 \qquad (1)$$

The ESR spectrum of **1** contains a broad line with no fine structure with a value of the *g* factor normally encountered in simple radical-anion salts of TCNQ ($g=2.0031$ for the solid, $g=2.0026$ for a solution in $CH_2Cl_2$, 290 K). In the IR spectrum, the $\nu$(CN) band appears as a doublet at 2150 and 2177 cm$^{-1}$, as compared with the unsplitted band at 2220 cm$^{-1}$ in the free TCNQ, which, again, is typical of a radical-ion [13].

The reaction with a large excess of TCNQ (upto 10 equiv.) yields the products of another stoichiometry (1:2) (**2** and **3**). They are green-coloured paramagnetic materials which have in their IR spectrum other bands in the $\nu$(CN) region (2130, 2150 and 2173 cm$^{-1}$). We suppose that complexes **2** and **3** belong to so-called 'complex salt' type and they can be formally described as $[Mo_3Y_7(dtc)_3]^+(TCNQ)^-\cdot TCNQ$. Complexes **2** and **3** are unstable in a solution of $CH_2Cl_2$ and **2** form **1** (eqn. (2)) if one attempts to recrystallize it:

$$2[Mo_3S_7(dtc)_3](TCNQ)_2=$$
$$[Mo_3S_7(dtc)_3]_2(TCNQ)_2+2TCNQ \qquad (2)$$

The structure of **1** is ionic. The $TCNQ^-$ anions are tied to centrosymmetrical dimers $(TCNQ^-)_2$ forming, with the two $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(dtc)_3]^+$ cations, dimeric $[Mo_3S_7(dtc)_3]_2(TCNQ)_2$ groups (Figs. 1 and 2). The bond lengths and angles in the cluster cation have normal values close to those found by us in

$[Mo_3S_7(dtc)_3]Cl$ (Tables 2 and 3) [15]. The average Mo–Mo bond length is 2.719(4) Å; the S–S bond length is 2.02–2.03(1) Å. The $S_2$ ligands are coordinated in the $\mu_2$-$\eta^2$:$\eta^2$ acetylene manner. The separation between the planes in the $(TCNQ^-)_2$ dimers is 3.16 Å. It should be noted that analogous dimers have been found in a number of structures of other salts (shown in parentheses is the separation in the dimer): $[Rh(2,6\text{-}Me_2C_6H_3)_4]TCNQ$ (3.1 Å) [2]; $[(\eta^6\text{-}C_6Me_6)_2M]\text{-}(TCNQ)_2$ (M = Fe, Ru; 3.23 Å) [4]; $[Pt(NH_3)_4](TCNQ)_2$ (3.12 Å) [5]: $[Nb_3Cl_6(\eta^6\text{-}C_6Me_6)_3](TCNQ)_2$ (3.10 Å) [7]; [Rb(18-crown-6)]TCNQ (3.23 Å) [16].

The most interesting feature in the structure of **1** is the presence of short cation–anion contacts: the nitrogen atoms of TCNQ are separated from the axial (relative to the $Mo_3$ plane) sulfurs of the $\mu_2$-$S_2$ ligands by distances that are considerably smaller than the sum of the sulfur and nitrogen van der Waals radii (3.44 Å [17]). Coordination of one of the nitrogens above the triangle defined by the axial S atoms almost on the extension of the S–S bonds (the S–S...N angle is 168°), is the usual one for the salts of the $[M_3X_7(LL)_3]^+$ cations (M = Mo, W; X = S, Se; LL = dtc [9, 15, 18]; M = Mo, Y = S, LL = $S_2P(OEt)_2$ [19]; M = Mo, Y = S, LL = $S_2PEt_2$ [20, 21]). This coordination type can be understood by assuming donation of the lone pair (e.g. Hal, S or N in this case) of the counter-anion to unoccupied $\sigma^*$-orbitals of the $Y_2^{2-}$ chalcogenide ligands. The latter are isolobal to $Hal_2$ molecules which form numerous adducts of $X_2 \cdot L$ type with different donors [22]. The coordination of another nitrogen, at only one of the three axial sulfurs on the side on the S–S bond, appears to us very unusual (the S–S...N angle is 124.6 Å). Authors of ref. 8 suppose that cation–anion contacts in TCNQ salts are actually sufficient to allow some kind of interaction (e.g. antiferromagnetic exchange) even on much greater distances (up to 3.6 Å).

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