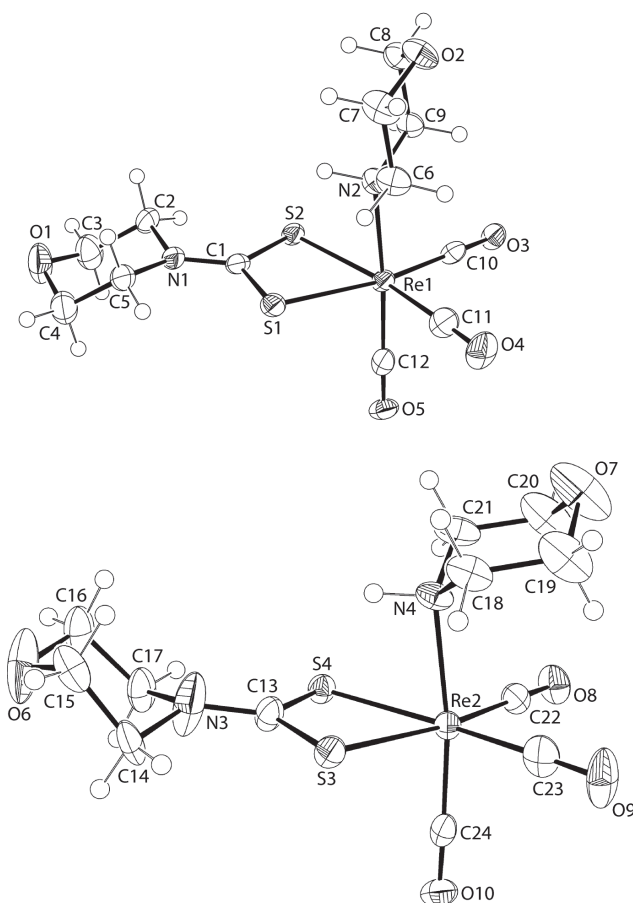


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# Crystal structure of *fac*-tricarbonyl-morpholine- $\kappa N$ -(morpholinocarbamodithioato- $\kappa^2 S, S'$ )rhenium(I), $C_{12}H_{17}N_2O_5ReS_2$



## Abstract

$C_{12}H_{17}N_2O_5ReS_2$ , monoclinic,  $P2_1/c$  (no. 14),  $a = 11.99393(5)$  Å,  $b = 20.48791(11)$  Å,  $c = 13.67105(6)$  Å,  $\beta = 103.3351(5)^\circ$ ,  $V = 3268.82(3)$  Å<sup>3</sup>,  $Z = 8$ ,  $R_{gt}(F) = 0.0238$ ,  $wR_{ref}(F^2) = 0.0629$ ,  $T = 100(2)$  K.

CCDC no.: 1945655

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.13 × 0.05 × 0.02 mm
Wavelength:	Cu K $\alpha$ radiation (1.54184 Å)
$\mu$ :	17.2 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$
$\theta_{max}$ , completeness:	67.1°, >99%
$N(hkl)_{measured}$ , $N(hkl)_{unique}$ , $R_{int}$ :	75890, 5849, 0.042
Criterion for $I_{obs}$ , $N(hkl)_{gt}$ :	$I_{obs} > 2 \sigma(I_{obs})$ , 5661
$N(param)_{refined}$ :	440
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

## Source of material

All chemicals and solvents were used as purchased without purification. The melting point was determined using a Melt-temp II digital melting point apparatus and was uncorrected. The solid-state IR spectrum was obtained on a Bruker Vertex 70v FTIR Spectrometer from 4000 to 400 cm<sup>-1</sup>. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at room temperature in DMSO-*d*<sub>6</sub> solution on a Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane. Bromopentacarbonylrhenium was prepared from the reaction of a 1:1 molar ratio of Re<sub>2</sub>(CO)<sub>10</sub> (Merck) and Br<sub>2</sub> (Panreac) in dichloromethane at 273 K. White solids were obtained from the slow evaporation of the solvent. The solids were recrystallised in acetone before use. The dithiocarbamate ligand was prepared *in situ* (methanol) from the reaction of CS<sub>2</sub>

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**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
Re1	0.48067(2)	0.73918(2)	0.62120(2)	0.02259(6)
S1	0.39428(8)	0.68948(5)	0.45420(7)	0.0261(2)
S2	0.61086(8)	0.65141(5)	0.58504(7)	0.0247(2)
O1	0.5279(3)	0.4847(2)	0.2837(3)	0.0533(10)
O2	0.6772(3)	0.91468(16)	0.4634(2)	0.0370(7)
O3	0.6276(2)	0.78483(16)	0.8243(2)	0.0308(7)
O4	0.2926(3)	0.8413(2)	0.6212(3)	0.0474(9)
O5	0.3492(2)	0.64913(17)	0.7346(2)	0.0324(7)
N1	0.5227(3)	0.59232(19)	0.4082(3)	0.0275(8)
N2	0.5747(3)	0.79975(18)	0.5290(3)	0.0258(7)
H2N	0.590(4)	0.7689(19)	0.477(3)	0.031*
C1	0.5112(3)	0.6384(2)	0.4735(3)	0.0252(8)
C2	0.6266(4)	0.5533(2)	0.4203(4)	0.0340(10)
H2A	0.667338	0.552236	0.492087	0.041*
H2B	0.678203	0.573008	0.381524	0.041*
C3	0.5958(5)	0.4855(3)	0.3839(4)	0.0466(13)
H3A	0.666842	0.460232	0.386927	0.056*
H3B	0.552957	0.464124	0.428894	0.056*
C4	0.4233(4)	0.5173(3)	0.2802(4)	0.0414(11)
H4A	0.382823	0.495944	0.327075	0.050*
H4B	0.373906	0.514226	0.211523	0.050*
C5	0.4442(4)	0.5871(2)	0.3085(3)	0.0335(10)
H5A	0.477960	0.609506	0.257953	0.040*
H5B	0.370675	0.608722	0.309498	0.040*
C6	0.5058(4)	0.8535(2)	0.4707(3)	0.0333(10)
H6A	0.483784	0.884955	0.517866	0.040*
H6B	0.434648	0.835152	0.427993	0.040*
C7	0.5715(4)	0.8888(3)	0.4052(4)	0.0415(12)
H7A	0.587890	0.858194	0.354188	0.050*
H7B	0.524059	0.924806	0.369422	0.050*
C8	0.7465(4)	0.8633(2)	0.5144(3)	0.0317(9)
H8A	0.819579	0.881451	0.553766	0.038*
H8B	0.764464	0.832376	0.464464	0.038*
C9	0.6864(3)	0.8270(2)	0.5842(3)	0.0270(9)
H9A	0.736124	0.791093	0.617492	0.032*
H9B	0.673459	0.857233	0.636986	0.032*
C10	0.5713(3)	0.7685(2)	0.7466(3)	0.0261(9)
C11	0.3640(4)	0.8039(3)	0.6214(3)	0.0356(11)
C12	0.3993(3)	0.6823(2)	0.6922(3)	0.0292(10)
Re2	0.01513(2)	0.82852(2)	0.81780(2)	0.02181(6)
S3	0.14641(8)	0.73251(5)	0.85210(8)	0.0263(2)
S4	−0.10187(8)	0.72578(5)	0.79761(8)	0.0248(2)
O7	0.0080(3)	0.9214(3)	1.1137(4)	0.0725(15)
O8	−0.1807(3)	0.92886(16)	0.7724(3)	0.0378(8)
O9	0.1889(3)	0.94130(17)	0.8542(4)	0.0554(11)
O10	0.0256(3)	0.82962(16)	0.5961(2)	0.0349(7)
N4	0.0112(3)	0.81202(19)	0.9809(3)	0.0276(8)
H4N	0.010(4)	0.7635(5)	0.981(4)	0.033*
C13	0.0261(4)	0.6835(2)	0.8313(4)	0.0317(10)
O6 <sup>a</sup>	0.0444(4)	0.48871(19)	0.8925(4)	0.0825(17)
N3 <sup>a</sup>	0.0316(4)	0.6191(2)	0.8434(6)	0.075(2)
C14 <sup>a</sup>	0.1338(7)	0.5786(4)	0.8489(8)	0.040(2)
H14A <sup>a</sup>	0.204486	0.605389	0.862979	0.047*
H14B <sup>a</sup>	0.128974	0.553867	0.785839	0.047*
C15 <sup>a</sup>	0.1300(8)	0.5336(4)	0.9358(7)	0.046(3)

**Table 2** (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
H15A <sup>a</sup>	0.204524	0.511544	0.960996	0.055*
H15B <sup>a</sup>	0.109065	0.557658	0.991787	0.055*
C16 <sup>a</sup>	−0.0663(6)	0.5248(4)	0.8848(8)	0.043(3)
H16A <sup>a</sup>	−0.067634	0.545782	0.949826	0.052*
H16B <sup>a</sup>	−0.132051	0.494501	0.866756	0.052*
C17 <sup>a</sup>	−0.0727(7)	0.5758(4)	0.8041(8)	0.041(2)
H17A <sup>a</sup>	−0.144512	0.601218	0.794586	0.049*
H17B <sup>a</sup>	−0.068759	0.555305	0.739383	0.049*
O6 <sup>b</sup>	0.0444(4)	0.48871(19)	0.8925(4)	0.0825(17)
N3 <sup>b</sup>	0.0316(4)	0.6191(2)	0.8434(6)	0.075(2)
C14 <sup>b</sup>	0.1437(8)	0.5946(5)	0.9098(10)	0.036(3)
H14C <sup>b</sup>	0.210063	0.619070	0.897010	0.043*
H14D <sup>b</sup>	0.143216	0.598053	0.981908	0.043*
C15 <sup>b</sup>	0.1458(10)	0.5250(5)	0.8779(12)	0.058(5)
H15C <sup>b</sup>	0.148332	0.523279	0.806074	0.070*
H15D <sup>b</sup>	0.216120	0.503810	0.917351	0.070*
C16 <sup>b</sup>	−0.0427(9)	0.5179(5)	0.8204(8)	0.047(4)
H16C <sup>b</sup>	−0.113306	0.491168	0.807344	0.057*
H16D <sup>b</sup>	−0.018777	0.524525	0.756474	0.057*
C17 <sup>b</sup>	−0.0609(10)	0.5822(5)	0.8676(11)	0.038(3)
H17C <sup>b</sup>	−0.136634	0.601342	0.836619	0.046*
H17D <sup>b</sup>	−0.052531	0.578250	0.941107	0.046*
C18	0.1134(4)	0.8333(3)	1.0592(4)	0.0358(11)
H18A	0.183929	0.823206	1.036187	0.043*
H18B	0.116227	0.808700	1.122071	0.043*
C19	0.1091(4)	0.9054(3)	1.0798(5)	0.0573(16)
H19A	0.177773	0.918175	1.131771	0.069*
H19B	0.109761	0.930179	1.017763	0.069*
C20	−0.0912(4)	0.9043(3)	1.0381(5)	0.0591(18)
H20A	−0.091440	0.929203	0.976068	0.071*
H20B	−0.160754	0.916386	1.061290	0.071*
C21	−0.0943(4)	0.8317(3)	1.0148(4)	0.0378(11)
H21A	−0.099035	0.806556	1.075635	0.045*
H21B	−0.163198	0.821541	0.961414	0.045*
C22	−0.1065(3)	0.8910(2)	0.7906(3)	0.0285(9)
C23	0.1239(4)	0.8982(2)	0.8422(4)	0.0380(11)
C24	0.0213(3)	0.83015(19)	0.6804(4)	0.0265(9)

<sup>a</sup>Occupancy: 0.578(10), <sup>b</sup>Occupancy: 0.422(10).

(Panreac 0.25 mmol) with morpholine (Merck, 0.25 mmol) and NaOH (0.02 mL; 50% w/v); CS<sub>2</sub> was added dropwise into the methanolic solution (15 mL). The resulting mixture was kept at 273 K for 0.5 h. Bromopentacarbonylrhenium (I) (0.25 mmol, 0.102 g) in methanol (10 mL) was added to the prepared sodium morpholinedithiocarbamate. The resulting mixture was stirred under reflux for 2 h. The filtrate was evaporated slowly until a yellow precipitate was formed. The precipitate was recrystallised from methanol-dichloromethane by slow evaporation to yield yellow crystals. Yield: 0.091 g, 70.1%; **M.pt.**: 493–495 K. **IR** (cm<sup>−1</sup>): 2006 (s) ν(CO), 1988(vs, br) ν(CO), 1511(s) ν(CN), 1112(s) ν(CO), 1024 (m) ν(CS), 999 ν(CS). **<sup>1</sup>H NMR** (DMSO-*d*<sub>6</sub>): δ 3.58–3.76 (m, 4H, CH<sub>2</sub>N), 3.78–3.82 (m, 4H, CH<sub>2</sub>O). **<sup>13</sup>C{<sup>1</sup>H} NMR** (DMSO-*d*<sub>6</sub>): δ

47.0 (C–N), 47.1 (C–N), 65.6 (C–O), 65.8 (C–O), 195.7 (C–S), 195.8, 211.4, 212.8 (CO).

### Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.99 Å) and refined as riding with  $U_{iso}(H) = 1.2U_{eq}(C)$ . The carbon atoms of the N3-morpholine ring were disordered over two positions. The O–C, N–C and C–C bond lengths were refined with distance restraints of  $1.41 \pm 0.01$ ,  $1.45 \pm 0.01$  and  $1.50 \pm 0.01$  Å, respectively. All atoms of the ring were refined anisotropically and the site occupancy of the major component refined to 0.578(10). Owing to poor agreement, two reflections, i.e. (2 0 0) and (–11 1 10), were omitted from the final cycles of refinement. The maximum and minimum residual electron density peaks of 2.89 and  $1.94 \text{ e Å}^{-3}$ , respectively, were located 0.78 and 0.66 Å from the Re1 atom, respectively.

### Comment

During on-going studies of the structural chemistry of binuclear molecules of the general formula  $[(CO)_3Re(S_2CNR_2)]_2$ , for R = Et [5], *n*-Pr [6] and *n*-Bu [7], crystalline side-products have been isolated whereby the incorporation of a coordinating solvent molecule results in the isolation of a mononuclear species, such as is the case of the recent report of the structure of  $(CO)_3Re(S_2CNMe_2)(N \equiv CMe)$  [8]. Herein, the crystal and molecular structures of a closely related species recently isolated in this research programme, namely  $(CO)_3Re[S_2CN(CH_2CH_2)_2O]N(CH_2CH_2)_2O$ , (I), are described.

Two independent molecules comprise the asymmetric unit of (I) and these are shown in the figure (50% displacement ellipsoids; for the second independent molecule, lower image, only the major component of the disorder is shown). In terms of the coordination geometry, the molecules are quite similar and each comprises a chelating dithiocarbamate ligand, three carbonyl groups and an nitrogen-bound morpholine molecule. The carbonyls occupy facial positions in the resultant  $C_3NS_2$  donor set which defines an approximate octahedral geometry. The dithiocarbamate ligand coordinates symmetrically with  $Re1-S1 = 2.4963(10)$  Å and  $Re1-S2 = 2.5044(10)$  Å, and this symmetry is reflected in the equivalence in the associated C–S bond lengths, that is  $C1-S1 = 1.720(4)$  Å and  $C1-S2 = 1.727(4)$  Å [for the Re2-containing molecule:  $Re2-S3 = 2.4956(10)$  Å,  $Re2-S4 = 2.5095(10)$  Å,  $C13-S3 = 1.727(5)$  Å and  $C13-S4 = 1.730(4)$  Å]. The Re–N bond lengths, i.e.  $Re1-N2 = 2.249(4)$  Å and  $Re2-N4 = 2.267(4)$  Å, are equal within experimental error. The deviations from the ideal geometry relate to the acute chelate angle [ $S1-Re1-S2 = 70.90(3)^\circ$  and  $S3-Re2-S4 = 70.86(3)^\circ$ ] and the maxi-

mum deviations in the trans angles are found in (carbonyl) C–Re–S(thiolate) angles in each independent molecule [ $C11-Re1-S2 = 168.43(13)^\circ$  and  $C22-Re2-S3 = 169.87(13)^\circ$ ]. From the figure, the most obvious difference between the structures is found in the relative orientations of the nitrogen-bound morpholine molecules; each has a chair conformation. To a first approximation, in the Re1-molecule this group can be considered orthogonal to the  $ReS_2C$  chelate ring but, parallel to the ring in the Re2-molecule and folded over towards the two carbonyl groups co-planar with the chelate ring. With reference to the six-membered morpholine ring, the Re1 occupies an axial position whereas the Re2 atom occupies an equatorial position. The observed coordination geometries in the title compound match literature precedents [8, 9].

The most prominent feature of the molecular packing is the formation of zig-zag (glide symmetry) supramolecular chains along the *c*-axis as the morpholine–N–H atoms participate in N–H $\cdots$ O(carbonyl) interactions [ $N2-H2n \cdots O3^i$ :  $H2n \cdots O3^i = 2.49(4)$  Å,  $N2 \cdots O3^i = 3.472(5)$  Å with an angle at  $H2n = 167(3)^\circ$  and  $N4-H4n \cdots O10^{ii}$ :  $H4n \cdots O10^{ii} = 2.45(3)$  Å,  $N4 \cdots O10^{ii} = 3.287(5)$  Å with angle at  $H4n = 141(4)^\circ$  for symmetry operations (i)  $x, 3/2 - y, -1/2 + z$  and (ii)  $x, 3/2 - y, 1/2 + z$ ]. The chains comprise Re1- or Re2-containing molecules exclusively. Globally, like-molecules assemble into layers and these stack, alternating along the *a*-axis. A substantial number of weak C–H $\cdots$ O(carbonyl) interactions are evident in the crystal. The most prominent contact in the layers comprising Re1-molecules are coordinated-morpholine–C–H $\cdots$ O(carbonyl) interactions [ $C7-H7b \cdots O1^{iii}$ :  $H7b \cdots O1^{iii} = 2.38$  Å,  $C7 \cdots O1^{iii} = 3.245(7)$  Å with angle at  $H7b = 145^\circ$  for (iii)  $1 - x, 1/2 + y, 1/2 - z$ ] and the closest interactions within the layers of Re2-containing molecules are of the type dithiocarbamate-morpholine–C–H $\cdots$ O(carbonyl) [ $C17-H17b \cdots O7^i$ :  $H17b \cdots O7^i = 2.18$  Å,  $C17 \cdots O7^i = 2.980(11)$  Å with angle at  $H17b = 137^\circ$ ]. The C–H $\cdots$ O contacts between layers involve dithiocarbamate-morpholine–C–H as the donors and occur between the independent molecules [ $C2-H2b \cdots O8^{iv}$ :  $H2b \cdots O8^{iv} = 2.50$  Å,  $C2 \cdots O8^{iv} = 3.423(6)$  Å with angle at  $H2b = 155^\circ$  for (iv)  $1 + x, 3/2 - y, -1/2 + z$  and  $C15-H15a \cdots O2^v$ :  $H15a \cdots O2^v = 2.52$  Å,  $C15 \cdots O2^v = 3.422(10)$  Å with angle at  $H15a = 152^\circ$  for (v)  $1 - x, -1/2 + y, 3/2 - z$ ].

The molecular packing was further analysed in terms of the calculation of the Hirshfeld surfaces as well the full and delineated two-dimensional fingerprint plots employing Crystal Explorer 17 [10] using established procedures [11]. This methodology has proved most successful in distinguishing the surface contributions in circumstances where multiple molecules comprise the asymmetric unit [12]. Entirely consistent with both hydrogen- and oxygen-rich regions in the molecules, as well as intermolecular N–H $\cdots$ O and C–H $\cdots$ O

contacts less than the sum of the respective van der Waals radii, the most significant contributions to the Hirshfeld surfaces of the Re1- and Re2-containing molecules come from H...O/O...H contacts at 40.9 and 43.2%, respectively. Next most significant are H...H contacts at 30.2 and 30.7%, respectively, with some contacts also within the sum of the van der Waals radii. The other major contributions to the Hirshfeld surfaces are from H...C/C...H [11.7 and 10.1%, respectively] and H...S/S...H [8.8 and 8.9%, respectively] contacts which, with the former occurring at distances at or beyond the respective sums of the van der Waals radii, respectively. The small but, different differences in the percentage contributions from the aforementioned contacts clearly differentiate between the independent molecules [12].

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## References

1. Rigaku Oxford Diffraction. CrysAlis<sup>PRO</sup>. Rigaku Corporation, Oxford, UK (2018).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **45** (2012) 849–854.
5. Lee, S. M.; Lo, K. M.; Heard, P. J.; Tiekink, E. R. T.: Redetermination of the crystal structure of bis( $\mu_2$ -di-ethylthiocarbamato- $\kappa^3$ S,S'; $\kappa^3$ S:S:S')-hexacarbonyl-di-rhenium(I), C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>Re<sub>2</sub>S<sub>4</sub>. *Z. Kristallogr. NCS* **234** (2019) 719–721.
6. Lo, K. M.; Lee, S. M.; Heard, P. J.; Tiekink, E. R. T.: Crystal structure of bis( $\mu_2$ -di-*n*-propylthiocarbamato- $\kappa^3$ S,S'; $\kappa^3$ S:S:S')-hexacarbonyl-di-rhenium(I), C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>O<sub>6</sub>Re<sub>2</sub>S<sub>4</sub>. *Z. Kristallogr. NCS* **234** (2019) doi: 10.1515/ncrs-2019-0489.
7. Heard, P. J.; Halcovitch, N. R.; Lee, S. M.; Tiekink, E. R. T.: Crystal structure of bis( $\mu_2$ -di-*n*-butylthiocarbamato- $\kappa^3$ S,S'; $\kappa^3$ S:S:S')-hexacarbonyl-di-rhenium(I), C<sub>24</sub>H<sub>36</sub>N<sub>2</sub>O<sub>6</sub>Re<sub>2</sub>. *Z. Kristallogr. NCS* **233** (2018) 485–487.
8. Tan, S. L.; Lee, S. M.; Heard, P. J.; Halcovitch, N. R.; Tiekink, E. R. T.: *fac*-Acetonitriletricarbonyl(dimethylcarbamodithioato- $\kappa^2$ S,S')rhenium(I): crystal structure and Hirshfeld surface analysis. *Acta Crystallogr. E* **73** (2017) 213–218.
9. Herrick, R. S.; Ziegler, C. J.; Sripathongnak, S.; Barone, N.; Costa, R.; Cupelo, W.; Gambella, A.: Preparation and characterization of rhenium(I) tricarbonyl dithiocarbamate compounds; Re(CO)<sub>3</sub>(S<sub>2</sub>CNMe<sub>2</sub>)(L). *J. Organomet. Chem.* **694** (2009) 3929–3934.
10. Turner, M. J.; Mckinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A.: Crystal Explorer v17. The University of Western Australia, Australia (2017).
11. Tan, S. L.; Jotani, M. M.; Tiekink, E. R. T.: Utilizing Hirshfeld surface calculations, non-covalent interaction (NCI) plots and the calculation of interaction energies in the analysis of molecular packing. *Acta Crystallogr. E* **75** (2019) 308–318.
12. Jotani, M. M.; Wardell, J. L.; Tiekink, E. R. T.: Supramolecular association in the triclinic ( $Z' = 1$ ) and monoclinic ( $Z' = 4$ ) polymorphs of 4-(4-acetylphenyl)piperazin-1-ium 2-amino-4-nitrobenzoate. *Z. Kristallogr. – Cryst. Mater.* **234** (2019) 43–57.